Defense Threat Reduction Agency
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Energetic Materials for Bio-Agent Destruction

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TECHNICAL REPORT

March 2017

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UNIT CONVERSION TABLE
U.S. customary units to and from international units of measurement[*]

U.S. Customary Units	Multiply by →	← Divide by[†]	International Units
Length/Area/Volume			
inch (in)	2.54	$\times 10^{-2}$	meter (m)
foot (ft)	3.048	$\times 10^{-1}$	meter (m)
yard (yd)	9.144	$\times 10^{-1}$	meter (m)
mile (mi, international)	1.609 344	$\times 10^{3}$	meter (m)
mile (nmi, nautical, U.S.)	1.852	$\times 10^{3}$	meter (m)
barn (b)	1	$\times 10^{-28}$	square meter (m^2)
gallon (gal, U.S. liquid)	3.785 412	$\times 10^{-3}$	cubic meter (m^3)
cubic foot (ft^3)	2.831 685	$\times 10^{-2}$	cubic meter (m^3)
Mass/Density			
pound (lb)	4.535 924	$\times 10^{-1}$	kilogram (kg)
unified atomic mass unit (amu)	1.660 539	$\times 10^{-27}$	kilogram (kg)
pound-mass per cubic foot (lb ft^{-3})	1.601 846	$\times 10^{1}$	kilogram per cubic meter (kg m^{-3})
pound-force (lbf avoirdupois)	4.448 222		newton (N)
Energy/Work/Power			
electron volt (eV)	1.602 177	$\times 10^{-19}$	joule (J)
erg	1	$\times 10^{-7}$	joule (J)
kiloton (kt) (TNT equivalent)	4.184	$\times 10^{12}$	joule (J)
British thermal unit (Btu) (thermochemical)	1.054 350	$\times 10^{3}$	joule (J)
foot-pound-force (ft lbf)	1.355 818		joule (J)
calorie (cal) (thermochemical)	4.184		joule (J)
Pressure			
atmosphere (atm)	1.013 250	$\times 10^{5}$	pascal (Pa)
pound force per square inch (psi)	6.984 757	$\times 10^{3}$	pascal (Pa)
Temperature			
degree Fahrenheit (^{o}F)	[T(^{o}F) − 32]/1.8		degree Celsius (^{o}C)
degree Fahrenheit (^{o}F)	[T(^{o}F) + 459.67]/1.8		kelvin (K)
Radiation			
curie (Ci) [activity of radionuclides]	3.7	$\times 10^{10}$	per second (s^{-1}) [becquerel (Bq)]
roentgen (R) [air exposure]	2.579 760	$\times 10^{-4}$	coulomb per kilogram (C kg^{-1})
rad [absorbed dose]	1	$\times 10^{-2}$	joule per kilogram (J kg^{-1}) [gray (Gy)]
rem [equivalent and effective dose]	1	$\times 10^{-2}$	joule per kilogram (J kg^{-1}) [sievert (Sv)]

[*]Specific details regarding the implementation of SI units may be viewed at http://www.bipm.org/en/si/.
[†]Multiply the U.S. customary unit by the factor to get the international unit. Divide the international unit by the factor to get the U.S. customary unit.

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Final Report

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ENERGETIC MATERIALS FOR BIO-AGENT DESTRUCTION

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D. YEAR IV

a) Iodine-containing compounds

ii) Objective

The objective of this work was to produce known energetic materials or design and produce new materials which upon detonation will destroy support/storage facilities while utilizing the gaseous products obtained from the blast to destroy any remaining harmful airborne agents. Theoretical or empirical calculations which permit prediction of the likelihood and desirability of synthesis of the proposed materials based on density, heat of formation and detonation properties aid markedly in providing selection of compounds to be submitted for further testing.

YEAR I

iii) Status of effort

Good progress is being made toward meeting the objectives of this work. Our synthetic routes are reasonably straightforward and we utilize Gaussian 03 methodology to estimate enthalpy of formation; after determining density with a pycnometer, detonation properties (pressure and velocity) are calculated using Explo 5 or Cheetah 6. Three families of compounds have been prepared, viz., i) pentafluorosulfanyl derivatives; ii) polyiodoazoles; and iii) polyiodoxyazoles. The compounds have been carefully characterized via ^{1}H, and ^{13}C (and sometimes ^{19}F) NMR and infrared spectral analysis, DSC (thermal stability), elemental analysis, and impact sensitivity. In keeping with the terms of the award, a subcontract was established with Indian Head to test two compounds for their efficacy as biocidal reagents. The number of compounds will be increased to three and five, respectively, during the second and third years. 2-(Pentafluorosulfanyl-1,2,3-triazol-1-yl)-bis-(N,N-tris(pentafluorosulfanyl-1,2,3-triazol-1-ylethyl)-ethanamine) and tetraiodofuran have been sent to Indian Head. The results are pending. Such results will be helpful in making go/no go decisions.

iv) Accomplished Under These Goals

a) Pentafluorosulfanyl derivatives

i) Pentafluorosulfanyl-substituted poly-1,2,3-triazole compounds

The synthesis and properties of dense pentafluorosulfanyl-substituted poly-1,2,3-triazole compounds was undertaken.[1] One sample, 2-(pentafluorosulfanyl-1,2,3-triazol-1-yl)-bis-(N,N-tris(pentafluorosulfanyl-1,2,3-triazol-1-ylethyl)-ethanamine) was submitted to Indian Head for testing of biocidal characteristics.

Synthesis

The syntheses of pentafluorosulfanyl-substituted poly-triazoles involve click reactions between organic azides and pentaflurosulfanyl acetylene. 1,3-Diazido-2-propanol, 2-azido-N, N-bis(2-azidoethyl) ethanamine and 1,3-diazido-2,2-bis(azidomethyl) propane (**1-3**) were synthesized based on literature preparations.[2]

1   **2**   **3**
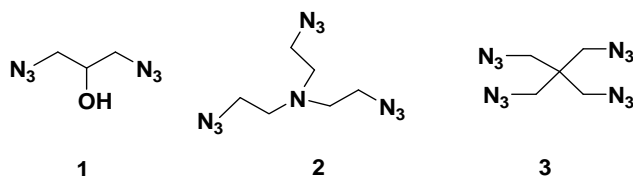
The synthesis of pentafluorosulfanyl acetylene was a challenging task since very low yields were obtained based on the literature method.[3] The procedure involves two steps: i) Addition of pentafluorosulfanyl bromide to acetylene; ii) Dehydro- bromination of 1-bromo-2-pentafluorosulfanyl ethene with KOH in petroleum ether. Due to fomation of water as a byproduct in the second step, aqueous KOH immediately reacts with the acidic proton of the desired product (pentafluorosulfsulfanyl acetylene) and results in the low yield obtained (10%). It is very difficult to remove the product quickly enough to avoid its contact with aqueous KOH.

$$SF_5Br \ + \ HC{\equiv}CH \ \xrightarrow{57^0C} \ SF_5\overset{H}{C}{=}CHBr$$

$$SF_5\overset{H}{C}{=}CHBr \ + \ KOH \ \xrightarrow{petroleum\ ether} \ SF_5C{\equiv}CH \ + \ H_2O \ + \ KBr$$
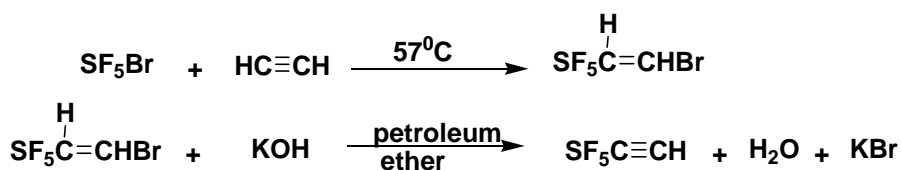
In order to obtain this compound in high yield, an alternative approach based on commerically avaliable pentafluorsulfanyl-tris-isopropylsilylacetylene was used. Desilylation of pentafluorsulfanyl-tris-isopropylsilylacetylene was carried out using triethylamine trihydrofluoride resulting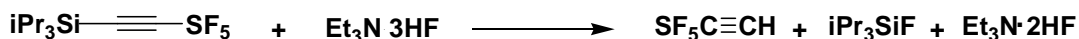 in pentafluorosulfanyl acetylene in good yield (60-65%).[4] The unfortunate drawback of this procedure is that the commercially avaliable pentafluorsulfanyl-tris-isopropylsilylacetylene is very expensive.

$$iPr_3Si{-}{\equiv}{-}SF_5 \ + \ Et_3N\ 3HF \ \longrightarrow \ SF_5C{\equiv}CH \ + \ iPr_3SiF \ + \ Et_3N{\cdot}2HF$$

Azides (**1-3**) were reacted with pentafluorosulfanyl acetylene in the presence of CuI (10 mol%) and 2,6-lutidine as catalyst to obtain the corresponding products (**1a-3a**) in moderate yields. Their properties are given in Table 1.
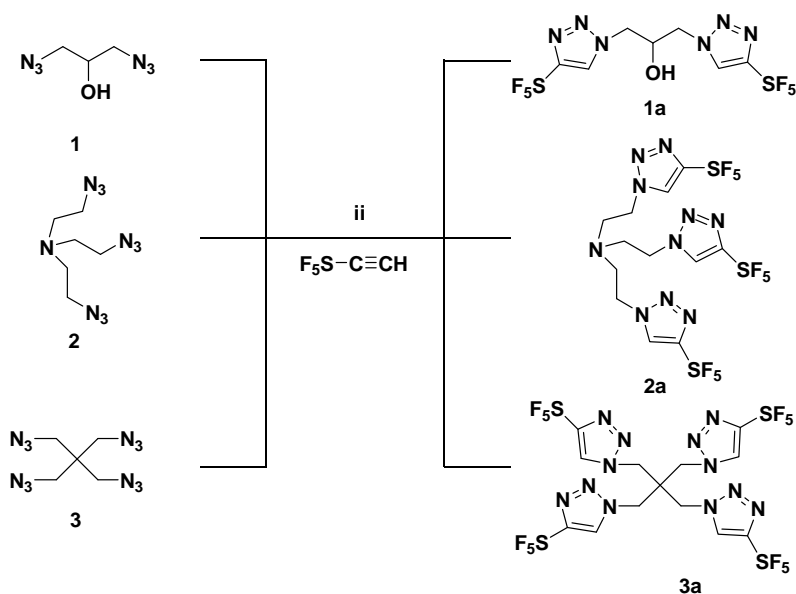
ii = CuI (10 mol %), 2,6-lutidine, CH₂Cl₂, RT

Table 1. Properties of pentafluorosulfanyl 1,2,3-triazoles

Compound	Yield [%]	$T_{dec.}$[a][°C]	d[b] [g cm^{-3}]	$\Delta H_f°$ [c] [kJ g^{-1}]	P [d] [GPa]	vD[e][m s^{-1}]	IS[f][J]
1a	55	305.2[g]	1.9	-3.5	16.58	6661	>40
2a	67	307.2	1.83	-2.96	17.82	6908	>40[i]
3a	73	343.5	1.94	-	-	-	>40
TNT	-	300	1.65	-	19.5	6881	15

[a] Thermal decomposition temperature under nitrogen gas (DSC, 5 °C min^{-1}); [b] From gas pycnometer (25 °C). [c] Heat of formation (calculated via Gaussian 03). [d]Calculated detonation pressure (Cheetah 4.0 & 5.0). [e] Calculated detonation velocity (Cheetah 4.0 & 5.0). [f] Impact sensitivity (BAM drophammer). [g] Thermal decomposition temperature under nitrogen gas (DSC, 10 °C min^{-1}). [i] Indian Head measurement: 141 cm (~66 J).

It should be noted that each of the SF$_5$-containing compounds has a thermal stability equivalent to or exceeding TNT and is considerably denser. Their calculated detonation properties approach those of TNT while they are more than 2.5 times less sensitive to impact than is TNT. It appears that they hold some promise for future use. Submission to Indian Head for testing will provide data on which to base go/no go decisions.

Work ongoing at Indian Head

Compound **2a** was selected for testing as an explosive (to be loaded with known AD metal mixture). Two and one-half grams of **2a** were submitted to Dr. Jillian Horn at Indian Head for testing which will include.

- Perform small scale safety testing.
- Run 'open' air blast test to measure pressure and temperature and reaction/burn time generated.
- Based on results of air blast, decide appropriateness of bug-kill test, and if so, which one.

To date (August 18, 2012) the following information has been provided by Indian Head.
- 141 cm impact (low sensitivity)
- 180 psig friction (low sensitivity)
- 0.165 Joules ESD (medium sensitivity)
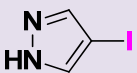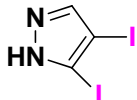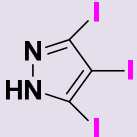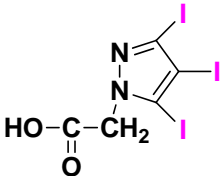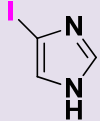
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4. G. S. Lal, Private Communication
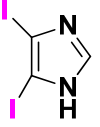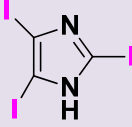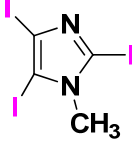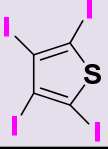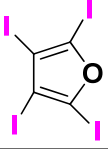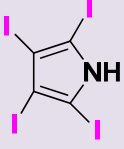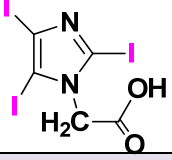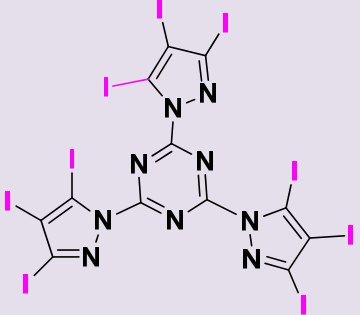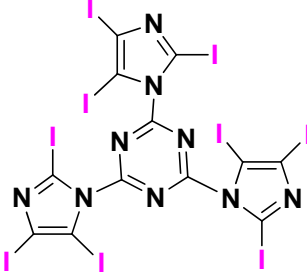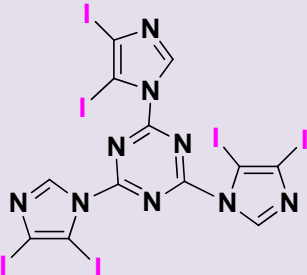
b) Iodine-containing compounds
i) Synthesis and characterization of iodo compounds

In order to achieve low pressure and prolonged high temperature detonations necessary to destroy storage facilities and bio-agents, 15 iodo compounds were prepared and characterized by IR, NMR, elemental analysis and differential scanning calorimetry (DSC). The physical properties are listed in Table 1; all the compounds possess a high content of iodine ranging between 65.4% and 89.0% as well as good densities falling in the 2.39 g/cm³ to 3.90 g/cm³ range. With the increase of iodine atom numbers in a single heterocyclic ring, the density increases; iodopyrazoles are more dense than their imidazole analogues. Most of the compounds exhibit good thermal stabilities (≥ 168 °C, Entry 11); compounds (entries 1-10) melt and then decompose while compounds (entries 11-15) decomposed without melting. The thermal stabilities of trisubstituted triazine compounds (entries 13-15) increase due to their symmetrical structure compared to their precursors. Impact sensitivity measurements were made using standard BAM techniques.[1] All of the compounds are impact insensitive (IS ≥28 J).

Table 1. Physical properties of iodo compounds

Entry	Structure	IS[a] (J)	Density [b] (g/cm³)	m.p. (°C) [c]	% Iodine
1		>40	2.48	109, 229 (decomp)	65.4
2		>40	3.14	160, 290 (decomp)	79.4
3		>40	3.38	220 282 (decomp)	85.4
4		>40	3.27	237, 247 (decomp)	75.6
5		>40	2.39	137, 220 (decomp)	65.4

6		>40	3.09	197, 233 (decomp)	79.4
7		>40	3.27	191, 252 (decomp)	85.4
8		>40	3.26	153, 318 (decomp)	82.8
9		>40	3.94	204, 397 (decomp)	86.4
10		35	3.83	163, 261 (decomp)	88.8
11		28	3.62	168 (decomp)	89.0
12		>40	3.00	180 (decomp)	75.6
13		>40	3.30	355 (decomp)	80.9

14		>40	3.10	315 (decomp)	80.8
15		>40	3.05	386 (decomp)	73.6

[a] Impact sensitivities measured by BAM drophammer; [b] Density, measured by gas pycnometer (25 °C); [c] Thermal decomposition temperature under nitrogen gas (DSC, 5 or 10 °C/min^{-1}).

Based on our experience, the introduction of a methyl group may help to reach the goal to decrease the energy as well as detonation pressure of energetic compounds; therefore, methyl and carboxylic acid groups were considered to lower detonation pressure and increase the gas products in the decomposition products. The results show that methyl derivatives lower the melting point and increase decomposition temperature while the presence of the carboxylic acid group decreases their thermal stabilities and densities to some extent but with small effect overall.

We believe that there is no information about the detonation properties of iodo compounds. Therefore, we selected two of the compounds with the highest iodine content (entries 10 and 11, Table 1) to evaluate energetic properties. To obtain their heats of formation, the Gaussian 03 (D.01)^2 program suite was employed, and isodesmic reactions were constructed (Scheme 1). The C, H, N, O atoms were optimized at

Scheme 1. Isodesmic reactions for iodo compounds

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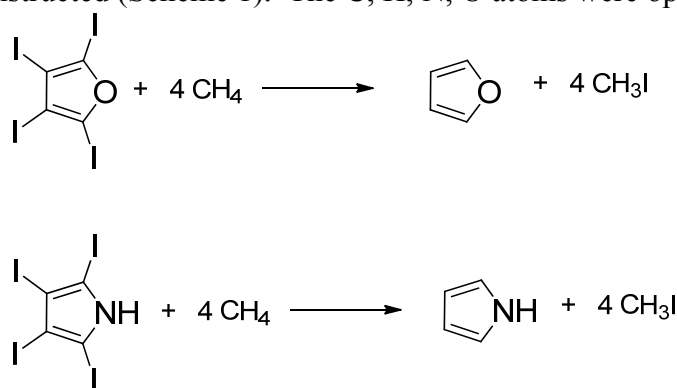
b3lyp/6-31g+ (d,p) level and iodine atoms at the Lanl2dz level. The heats of formation are summarized in Table 2. By using the experimental value of the densities, the detonation properties were calculated by Cheetah 6.0 (Table 2). Both compounds have low detonation velocities and pressures compared to traditional explosives. The high iodine content should form various iodine-containing species after decomposition which will be biocidal.

Table 2. Detonation properties of selected iodo compounds

Compd	HoF [a] (kJ/mol)	Density[b] (g/cm^3)	D[c] (m/s)	P[d] (Gpa)
Tetraiodofuran	264.3	3.83	2248	3.55
Tetraiodopyrrole	326.4	3.62	2009	2.42

[a] Heat of formation calculated with Gaussian 03; [b] Density, measured by gas pycnometer (25 °C); [c] Calculated detonation velocities - Cheetah 6.0; [d] Calculated detonation pressures - Cheetah 6.0.

Work ongoing at Indian Head

Tetraiodofuran (Entry 10, Table 1) was selected for testing (AD mix on the outside).   2.65 grams of tetraiodofuran were submitted to Dr. Jillian Horn at Indian Head for testing which will include.

- Perform small scale safety testing.
- Run 'open' air blast test to measure pressure and temperature and reaction/burn time generated.
- Based on results of air blast, decide appropriateness of bug-kill test, and if so, which one.

To date (August 18, 2012) the following information has been provided by Indian Head.

- Greater than 320 cm impact (low sensitivity)
- 235 psig friction (low sensitivity)
- 0.165 Joules ESD (medium sensitivity)

In summary, a series of iodo compounds were prepared and characterized, their densities and impact sensitivities were measured; two of the compounds with the highest iodine content were chosen to calculate the detonation properties. The results show that they should be the candidates for bio-agent destruction. Tetraiodofuran was sent to Indian Head for biocidal testing.

Synthetic procedures

4, 5-Diiodoimiazole:[3] Prepared according to the literature method; recrystallized from EtOH and water, yield 42%. M.p.: 197 – 198 °C, ^{1}H NMR (DMSO-d_6): 12.90, 7.77; IR (KBr): 3078, 2960, 2776, 2648, 2584, 2480, 1812, 1639, 1542, 1454, 1285, 1271, 1179, 1152, 955, 918, 818, 654, 620 cm^{-1}.
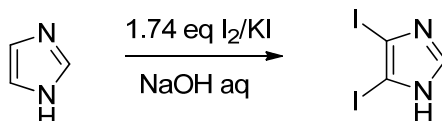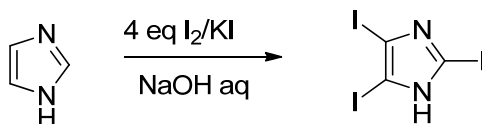
2,4,5-Triiodoimidazole:[3] Prepared according to the literature method using 4 equivalents I_2; recrystallized from 95% EtOH, yield 90%. M.p.: 191°C, ^{1}H NMR (DMSO-d_6): 13.34; IR (KBr): 3421, 3026, 2930, 2831, 2741, 2644, 2583, 1503, 1374, 1269, 1161, 971, 656, 436 cm^{-1}.
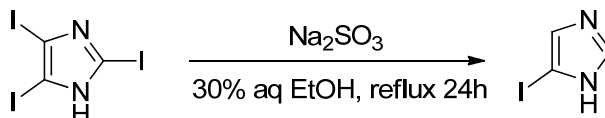
4(5)-Iodoimidazole:[4] Yield 93%. M.p.: 137°C, ^{1}H NMR (DMSO-d_6): 7.31, 7.62; IR (KBr): 3442, 3105, 2997, 2875, 2805, 2683, 2641, 2600, 1795, 1435, 1291, 1166, 1128, 1070, 955, 820, 620, 495 cm^{-1}.
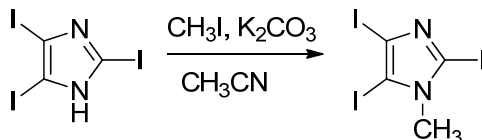
1-Methyl-2,4,5-triiodoimidazole: Modification of a described procedure,[5] potassium carbonate (0.61 g, 4.4 mmol) and 2,4,5-triiodoimidazole (0.90 g, 2 mmol) was added to 10 mL CH$_3$CN; 0.14 mL (2.2 mmol) CH$_3$I was then added slowly to the above mixture. The reaction mixture was stirred overnight, poured into 30 g ice water, filtered, and dried to 0.88 g white solid, yield 95%. M.p.: 153°C, ^{1}H NMR (DMSO-d_6): 3.65; ^{13}C NMR (DMSO-d_6): 39.33, 88. 49, 94.74, 97.50; IR (KBr): 2932, 1431, 1373, 1343, 1190, 1099, 1067, 947, 706,422 cm^{-1}. Elemental analysis: calcd for C$_3$H$_3$I$_3$N$_2$: C 10.45, H 0.66, N 6.09; found: C 10.47, H 0.60, N 5.80.
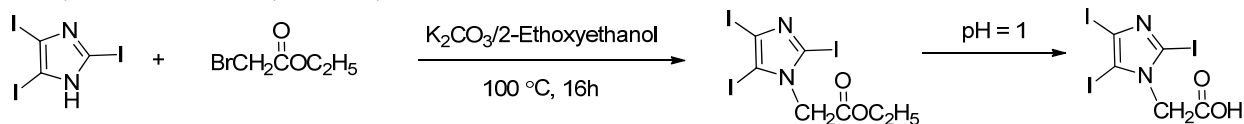
2,4,5-Triiodoimidazolyl-1-acetic acid: A mixture of potassium carbonate (0.61 g, 4.4 mmol), 2,4,5-triiodoimidazole (0.90 g, 2 mmol), and bromoacetate (2.2 mmol) in 25 mL 2-ethoxyethanol was heated at 100 °C for 16h. The suspension was filtered and the filtrate was evaporated under reduced pressure. The residue was dissolved in water, the solution was filtered and the filtrate acidified to pH 1 to obtain 2,4,5-triiodoimidazolyl-1-acetic acid, 0.75 g, yield 69%. M.p. 179 °C (dec), ^{1}H NMR (DMSO-d_6): 4.79, 13.53; IR

11

(KBr): 3427, 1717, 1458, 1418, 1356, 1328, 1238, 1173, 982, 889, 803, 669, 446 cm^{-1}. Elemental analysis: calcd for $C_5H_3I_3N_2O_2$: C 11.92, H 0.60, N 5.56; found: C 12.04, H 0.63, N 5.48.
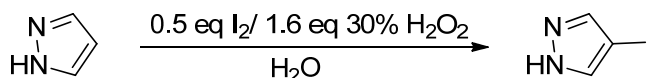
4-Iodopyrazole:[6] Prepared according to the literature method, yield 65%. M.p.: 109 °C, ^{1}H NMR (DMSO-d$_6$): 13.13, 7.77; IR (KBr): 3115, 3040, 2954, 2911, 2846, 1533, 1364, 1321, 1261, 1175, 1142,1032, 935, 872, 811, 649, 608 cm^{-1}.

76%   12%
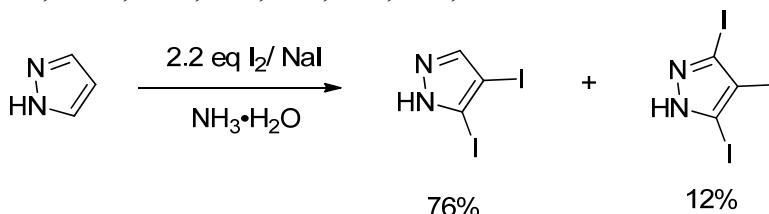
4, 5-Diiodopyrazole:[7] Prepared according to the literature method; the product was washed with aqueous ammonia and air dried, yield 40%. M.p.: 160 °C, ^{1}H NMR (DMSO-d$_6$): 13.49, 7.83; IR (KBr): 3126, 3022, 2926, 2850, 2781, 2709, 1323, 1254, 1175, 1059, 968, 942, 854, 806, 604 cm^{-1}.

3,4,5-Triiodopyrazole:[7] Yield 10%. M.p.: 220 °C, ^{1}H NMR (DMSO-d$_6$): 13.94; IR (KBr): 3073, 2949, 2872, 2816, 27311512, 1315, 1242, 1131, 961, 854, 807, 604, 447 cm^{-1}.
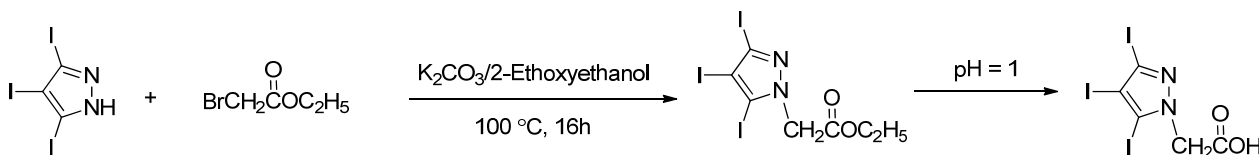
3, 4, 5-Triiodopyrazolyl-1-acetic acid: Similar method for preparing 2, 4, 5-triiodoimiazolyl-1-acetic acid, yield, 72%. ^{1}H NMR (DMSO-d$_6$): 13.48, 5.09; Elemental analysis: calcd for $C_5H_3I_3N_2O_2$: C 11.92, H 0.60, N 5.56; found: C 12.46, H 0.64, N 5.36.
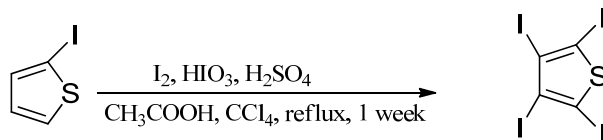
Tetraiodothiophene:[8] Start from 2-iodothiophene using a modified method, yield: 85%. M.p.: 203 °C, IR (KBr): 1648,1433, 1362, 1219, 1169, 1027, 954, 696 cm^{-1}. Elemental analysis: calcd for C_4I_4S: , C, 8.17; H, 0; N, 0; found: C, 8.14; H, 0; N, 0.78.
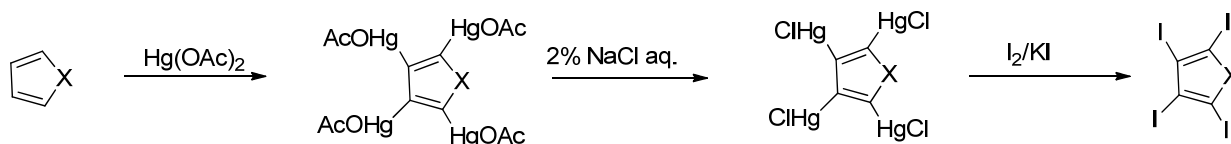
X=O, NH

Tetraiodopyrrole:[9] Prepared according to the literature method, yield: 47%. M.p. 168 °C (dec), ^{1}H NMR (DMSO-d$_6$): 12.3; ^{13}C NMR (DMSO-d$_6$): 86.7; 79.7. IR (KBr): 3431, 1530, 1375, 1292, 1170, 1027, 963, 897, 865, 772, 667 cm^{-1}. Elemental analysis: calcd for C$_4$HI$_4$N: C, 8.42; H, 0.18; N, 2.45, found: C, 8.68; H, 0.17; N, 2.46.

Tetraiodofuran: The same method to make tetraiodopyrrole, yield: 52%. M.p. 163 °C, ^{13}C NMR (DMSO-d$_6$): 106.2; 94.1; IR (KBr): 1700, 1497, 1444, 1242, 1084, 962, cm^{-1}.Elemental analysis: calcd for C$_4$HI$_4$N: C, 8.40; H, 0; N, 0, found: C, 8.38; H, 0.03; N, 0.10.
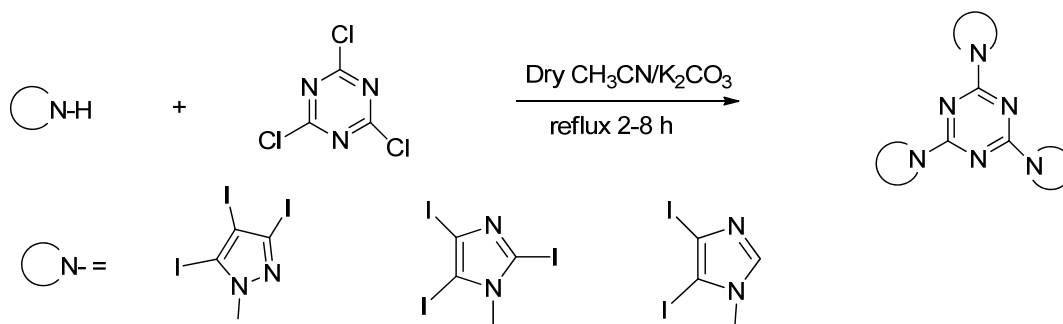
General procedure for preparing **tris (3, 4, 5-triiodopyraolyl)-2, 4, 6-triazine**, **tris (2, 4, 5-triiodoimidazolyl)-2, 4, 6-triazine** and **tris (4, 5-diiodoimidazolyl)-2, 4, 6-triazine**: the iodo compound (3.5 eq) and potassium carbonate (7.7 eq) were refluxed in CH$_3$CN for 1 h, then cyanuric chloride (1 eq) was added in small portions. Heating was continued for 2-8 h to finish the reaction. The reaction mixture was cooled to room temperature, filtered and the filter cake was washed with CH$_3$CN, followed by water, and air dried to obtained the expected product.

Tris (3, 4, 5-triiodopyraolyl)-2, 4, 6-triazine: yield 80%. M.p.: 355 °C (dec), ^{13}C NMR (DMSO-d$_6$): 162.9; 118.0; 98.56; 98.50; Elemental analysis: calcd for C$_{12}$I$_9$N$_9$: C 10.21, H 0, N 8.93; found: C 10.49, H 0.11, N 8.08.

Tris (2, 4, 5-triiodoimidazolyl)-2, 4, 6-triazine: yield 85%. M.p.: 315 °C (dec), ^{13}C NMR (DMSO-d$_6$): 162.4; 106.1; 95.2; 86.6; IR (KBr): 1547, 1456, 1382, 1274, 1163, 1065, 945, 808, 688, 648 cm^{-1}. Elemental analysis: calcd for C$_{12}$I$_9$N$_9$: C 10.21, H 0, N 8.93; found: C 10.23, H 0.02, N 8.57.

Tris (4, 5-diiodoimidazolyl)-2, 4, 6-triazine: yield 73%. M.p.: 386 °C (dec), ^{1}H NMR (DMSO-d$_6$): 9.00 ppm; ^{13}C NMR (DMSO-d$_6$): 39.33, 88. 49, 94.74, 97.50; Elemental analysis: calcd for C$_{12}$H$_3$I$_6$N$_9$: C 13.93, H 0.29, N 12.18; found: C 14.24, H 0.31, N 11.89.

References

1. a) www.bam.de. b) A portion (20 mg) of an iodo compound was subjected to a drop-hammer test using a 5 or 10 kg weight. The range in impact sensitivities according to the UN Recommendations is: insensitive >40 J; less sensitive >=35 J; sensitive >4 J; very sensitive <=3 J.

2. Gaussian 03, Revision D.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, Gomperts, J.; R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. Gaussian, Inc., Wallingford CT, **2004**.

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ii) Synthesis and characterization of iodoxy compounds

Although explosions of iodoxy compounds have been reported in the literature,[1] those compounds have not been studied as energetic materials. The densities of 1, 2, 4-triazolium periodate (density, 2.62 g/cm^3) and guanidinium periodate (density, 2.59 g/cm^3) suggest that such oxohalogens should exhibit useful attributes with higher densities than the perchlorates and also exhibit greater effectiveness toward bio-agents. The imidazole and pyrazole-based energetic compounds attract great interest for their good thermal stabilities and sensitivities. We have synthesized several kinds of imidazole or pyrazole-based iodo compounds (vide supra). Imidazole or pyrazole-based iodoxy compounds might be of interest for their high densities and thermal stabilities. Therefore, six different iodoxy compounds were synthesized and characterized by IR, and NMR spectra, elemental analysis, and differential scanning calorimetry (DSC). Additionally their detonation properties were calculated and are discussed below.

The most common oxidants that were used for the preparation of iodylarenes from iodoarenes include sodium hypochlorite, sodium periodate, dimethyldioxirane, and Oxone.[2] Since Oxone is a commercially available low cost reagent as well as having a good stability, simple handling and non-toxic nature, it was used for preparing iodoxy compounds using a modified method (Table 3).[2b] For mono iodo (Table 3, entry 3) compounds, the oxidation can be completed at room temperature using 1.3 eq Oxone. The formation of polyiodo compounds requires heating to 70 °C and extended reaction time was needed to finish the reaction. The N-nitration of imidazole or pyrazole could be achieved under mild conditions using 100% nitric acid and acetic anhydride,[3] while only 100% nitric acid was needed to prepare N-nitro iodoxy compounds in our work. All the compounds were confirmed by elemental analysis. NMR data could not be obtained for 3, 4-di-iodoxypyrazole and 3, 4, 5-triiodoxypyrazole because of their very low solubility in organic solvents.

Table 3. Synthesis of iodoxy compounds

Entry	Substrate	Product	Oxone	Reaction Temp. (°C)	Reaction Time (hr)	Yield (%)
1			2.6 eq	70	3	75.5
2			3.9 eq	70	6	55.6
3			1.3 eq	25	3	46.2
4			2.6 eq	70	6	75.5
5			3.9 eq	70	10	54.8

The impact sensitivities of the iodoxy compounds (Table 4) range between 2 to 40 J. 4,5-Di-iodoxyimidazole hemihydrate (Table 4, entry 1) shows an unusually low impact insensitivity which may result from the presence of the water in molecule which helps to form extensive hydrogen bonds and improve its impact sensitivity dramatically.

The hemihydrate of N-nitro-4-iodoxypyrazole (Table 4, entry 6) also improves the impact sensitivity to some extent. For pyrazole iodoxy derivatives, the greater number of the iodoxy substituents, the less impact sensitive the compound. The thermal stabilities of the compounds were studied by differential scanning calorimetry (DSC). All iodoxy compounds decomposed between 159 – 227 °C. The 3,4,5-tri-iodoxypyrazole (Table 4, entry 5) is the least thermally stable while 4,5-di-iodoxyimidazole hemidyrate (Table 4, entry 1) decomposed at 227 °C. As one of the most important physical properties of energetic compounds, the densities of iodoxy compounds were determined by using a gas pycnometer at 25 °C. The densities range between 2.54 – 3.68 g·cm^{-3}. 4-Iodoxypyrazole (Table 4, entry 3) has a higher density then diiodoxypyrazole (Table 4, entry 4) which may arise from the existence of the intramolecular hydrogen bond between O10 and H5 (2.821 Å Figure 1, dashed line) based on the optimized structure calculated using the Gaussian 03 suite of programs.
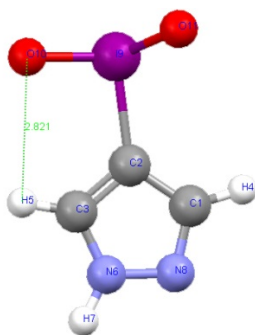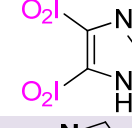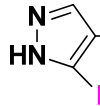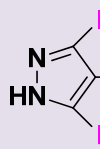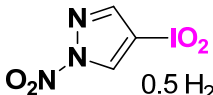
Figure 1. Optimized structure of 4-iodoxypyrazole

Table 4. Physical properties of iodoxy compounds

Entry	Structure	m.p^a (°C)	D^b (g/cm^3)	$\Delta H_f^{\circ\ c}$ (kJ/mol)	D^d (m/s)	P^e (Gpa)	IS^f (J)
1	O$_2$I-, N, N-H, 0.5 H$_2$O	227	2.85	-431	4461	11.86	>40
2	O$_2$I-, N-IO$_2$, N-H	183	3.68	-712	4891	16.98	5
3	N, HN-, IO$_2$	201	2.99	-64.8	-	-	2
4	N, HN-, IO$_2$, IO$_2$	188	2.87	-379	4181	10.24	4
5	IO$_2$, N, HN-, IO$_2$, IO$_2$	159	3.54	-690	4690	15.21	7

6	(structure: pyrazole with IO_2, O_2N, $0.5 H_2O$)	179	2.54	54.7	6897	28.33	12

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[a] Thermal decomposition temperature under nitrogen gas (DSC, 5 °C/min^{-1}); [b] Density, measured by gas pycnometer (25 °C); [c] Heat of formation calculated with Gaussian 03; [d] Calculated detonation velocities with Cheetah 6.0; [e] Calculated detonation pressures with Cheetah 6.0; [f] Impact sensitivities measured with a BAM drophammer.

The heats of formation for iodoxy compounds were calculated by using the Gaussian 03 suite of programs[4] by constructing isodesmic reactions (Figure 3) and are
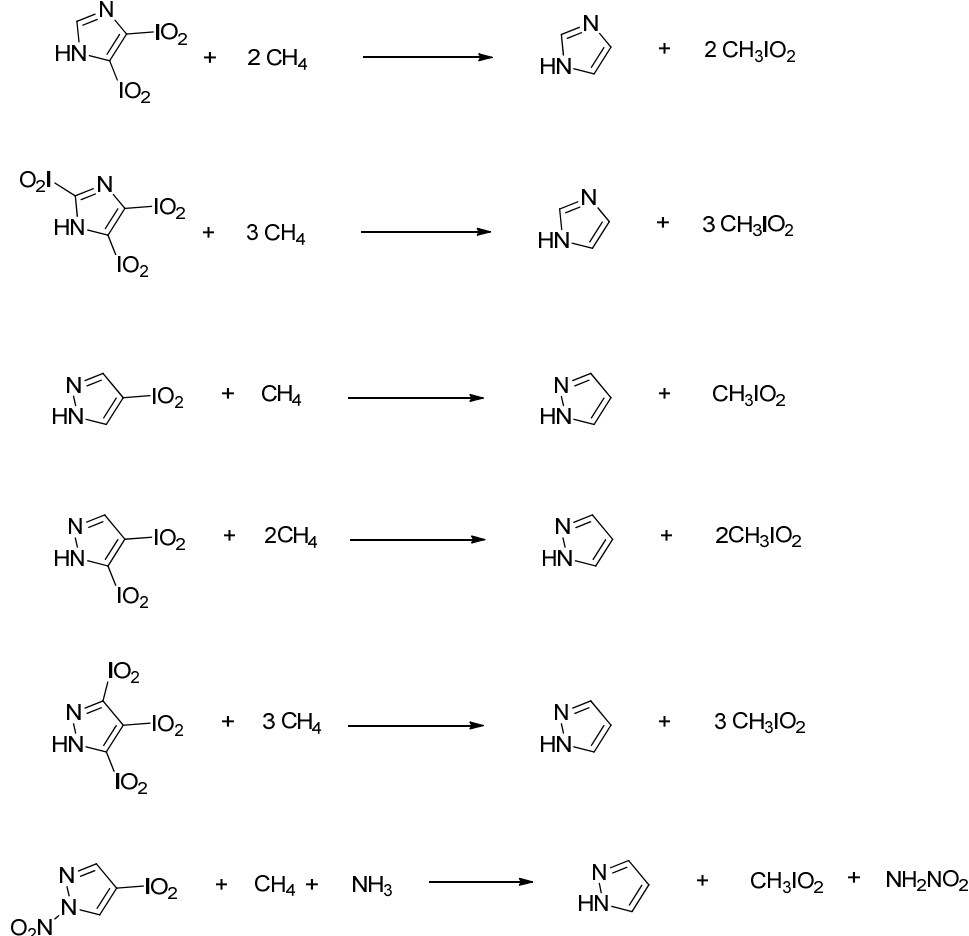
Figure 3.   Isodesmic reactions for iodoxy compounds

summarized in Table 4. The iodine atoms were optimized via mp2(full)/6-31g(d) at the ECP level, and the heat of formation of CH_3IO_2 was calculated using G2ECP (ZPE=MP2) methodology[5] and for other small molecules were obtained by employing the G2 method.. All the compounds exhibit negative heats of formation except N-nitro-4-iodoxypyrazole which has a positive value of 54.7 kJ/mol. By using the calculated values of the heats of formation and the experimental values for the densities, the detonation velocities (*D*) and detonation pressures (*P*) were calculated using the Cheetah 6.0 program. No detonation properties can be obtained for 4-iodopyrazole since it did not converge during the calculation. All the compounds have low detonation pressures that

range between 10.24 to 28.33 GPa and velocities lie between 4181 to 6897 m/s compared to the traditional energetic compounds but higher than iodo compounds. The detonation properties improve as the number of iodoxy group increases. The N-nitro group enhances the detonation properties markedly but also decreases the density.

In summary, six iodoxy compounds were synthesized in moderate yields by using straightforward methods. All the compounds were confirmed by elemental analysis and characterized by IR, ^{1}H and ^{13}C NMR, elemental analysis, and differential scanning calorimetry (DSC). Detonation properties were calculated. The unique high density, high iodine content and low detonation property of iodoxy compounds makes them interesting in some special energetic fields. The good thermal stability, moderate detonation properties and impact insensitiveness of 4, 5-diiodoxyimidazole hemidyrate makes it a candidate for a low pressure bio-agent addictive.

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YEAR II

iii) Accomplished under these goals

Good progress continues to be made toward meeting the objective of this work. Our synthetic routes are reasonably straightforward and we utilize Gaussian 03 methodology to estimate enthalpy of formation; after determining the experimental density with a pycnometer, detonation properties (pressure and velocity) are calculated using Explo 5 or Cheetah 6. Four families of compounds have been prepared, viz., i) polyiodoheterocycles; ii) polyiodoxyazoles (terminated in second year); iii) polyiodides, and iv) pentafluorosulfanyl derivatives (terminated in second year); The compounds have been carefully characterized via ^{1}H, and ^{13}C (and sometimes ^{15}N) NMR and infrared spectral analysis, DSC (thermal stability), elemental analysis, and impact sensitivity. In keeping with the terms of the award, a subcontract was established with Indian Head to test compounds for their efficacy as biocidal reagents. China Lake has also been involved in this testing. Based on the results obtained from preliminary testing of 2-(pentafluorosulfanyl-1,2,3-triazol-1-yl)-bis-(N,N-tris(pentafluorosulfanyl-1,2,3-triazol-1-ylethyl)-ethanamine) and tetraiodo furan at Indian Head, the latter was down selected for formulation studies which were initially carried out at China Lake. The results are very encouraging. The compound has been transitioned to 6.2 for further study at China Lake, Indian Head and Elgin.

a) Iodine-containing compounds
i) Synthesis and characterization of iodo compounds

(See Appendix A for full length paper – He, C.; Zhang, J.; Shreeve, J. M. *Chemistry – a European Journal,* **2013**, *19*, 7503-7509

In order to achieve low pressure and prolonged high temperature detonations necessary to destroy storage facilities and bio-agents, 15 iodo compounds were prepared and characterized by IR, NMR, elemental analysis and differential scanning calorimetry (DSC). The physical properties are listed in Table 1 (Appendix A); all of the compounds possess a high content of iodine ranging between 65.4% and 89.0% as well as good densities falling in the 2.39 g/cm^3 to 3.90 g/cm^3 range. With the increase of iodine atom numbers in a single heterocyclic ring, the density increases; iodopyrazoles are more dense than their imidazole analogues. Most of the compounds exhibit good thermal stabilities ($\geq$ 168 °C, entry 11); compounds - entries 1-10 - melt and then decompose while compounds - entries 11-15 - decompose without melting. The thermal stabilities of trisubstituted triazine compounds - entries 13-15 - increase due to their symmetrical structure compared to their precursors. Impact sensitivity measurements were made using standard BAM techniques.[1] All of the compounds are impact insensitive (IS $\geq$28 J).

We believe that there is no information about the detonation properties of iodo compounds. Therefore, we selected two of the compounds with the highest iodine content (entries 10 and 11, Table 1 – Appendix A) to evaluate energetic properties. To obtain their heats of formation, the Gaussian 03 (D.01)[2] program suite was employed, and isodesmic reactions were constructed (Scheme 1). The C, H, N, O atoms were optimized at b3lyp/6-31g+ (d,p) level and iodine atoms at the Lanl2dz level. The heats of formation are summarized in Table 1 below. By using the experimental value of the densities, the detonation properties were calculated by Cheetah 6.0 (Table 1 – Appendix A). Both

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compounds have low detonation velocities and pressures compared to traditional explosives. The high iodine content should form various iodine-containing species after decomposition which will be biocidal.
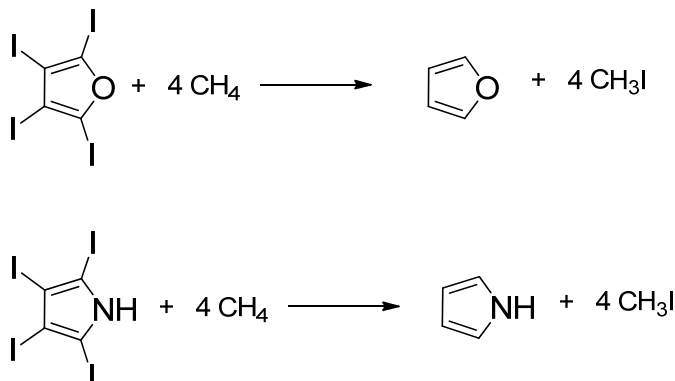
Scheme 1. Isodesmic reactions for iodo compounds

Table 1. Detonation properties of selected iodo compounds

Compd	HoF [a] (kJ/mol)	Density[b] (g/cm^3)	D^c (m/s)	P^d (Gpa)
Tetraiodofuran	264.3	3.83	2248	3.55
Tetraiodopyrrole	326.4	3.62	2009	2.42

[a] Heat of formation calculated with Gaussian 03; [b] Density, measured by gas pycnometer (25 °C); [c] Calculated detonation velocities - Cheetah 6.0; [d] Calculated detonation pressures - Cheetah 6.0.

Work at Indian Head/China Lake

In spring 2012, tetraiodofuran (TIF) was selected for testing (AD mix on the outside). Therefore, TIF were submitted to Dr. Jillian Horn at Indian Head for testing which included:

- Perform small scale safety testing.
- Run 'open' air blast test to measure pressure and temperature and reaction/burn time generated.
- Based on results of air blast, decide appropriateness of bug-kill test, and if so, which one.

In August 2012 the following information was provided by Indian Head:

- Greater than 320 cm impact (low sensitivity)
- 235 psig friction (low sensitivity)
- 0.165 Joules ESD (medium sensitivity)

Dr. Su Peiris, GOR, in discussion with others, determined that TIF was suitable for further biocidal testing. Therefore, additional amounts of TIF were synthesized and submitted as detailed below:

Dr. Jillian Horn, Indian Head, MD   68 g

Dr. Curt Johnson, China Lake, CA   104 g   (90 g returned to UI)

Dr. Jim Lightstone, Indian Head, MD 66g

Formulation tests were undertaken at China Lake using a purified sample of TIF (vide infra). The remainder of TIF was returned to UI for further purification. The purified sample was then forwarded to Dr. Jim Lightstone at Indian Head for biocidal testing.

The results at China Lake on TIF as reported to us are <u>reproduced</u> exactly in the following.[3] For further details, the report by Dr. Curtis Johnson, NAWCWD should be consulted.

"Tetraiodofuran Characterization"
Kelvin Higa and Curtis Johnson, NAWCWD, 19 April 2013

This brief report describes tests of the 104 g TIF sample received from U. Idaho 15 April 2013.

1. Booster Test of $Al(H2^*)/Bi(IO_3)_3/TIF$. The Booster Test is a NAWCWD method to interrogate sample composite reactivity. A 50:50 mixture composed of a "test sample" and $Al(80nm)/MoO_3(45nm)$ nanothermite is prepared, ~15 mg of the mixture is placed on an inverted Al weighing pan, and the mixture ignited with a spark. The dent in the pan (that forms in ~200 μs) is measured, and the dent attributed to the Al/MoO_3 is subtracted out to determine the deflection attributed to the test sample (in mm/g). Loading levels between 0 and 50% of TIF and C_2I_4 in the test sample were evaluated (see Figure 1 below). $Al(H2^*)$, activated aluminum, is Valimet H-2 Al powder coated with 5% $K_2AlF_5 \cdot H_2O$.

Both TIF and C_2I_4 permitted high loading levels with very little change in the deflection value for the $Al(H2^*)/Bi(IO_3)_3/I_2$ Source composites. These results suggest that the amount of TIF or C_2I_4 could be varied over a wide range without imposing a large effect on the reactivity of the $Al(H2^*)/Bi(IO_3)_3$ thermite (i.e., in tests at NSWC-IHD).

Booster Test for Al(H2*)/Bi(IO$_3$)$_3$/I$_2$ Source

Based on the earlier work carried out at Indian Head involving a non idealized formulation, a briefing presented by the Assistant Secretary of Defense for Research and Engineering to the House Armed Services Committee contained the following:

"Defense Threat Reduction Agency funded basic research at University of Idaho and two Navy Warfare Center Labs have resulted in the development of new materials for defeating targets that contain biological agents. Weapon payloads using these materials employ the dual kill mechanisms of heat and chemistry. The addition of long-burning metals, e.g., Al, and iodine-forming chemicals to the payload increases the temperature during the blast and produces iodine gas to prolong the kill of biological agents in the post-blast plume."

TIF and its properties.

Synthetic procedure

Tetraiodofuran[4]: Yield: 52%. M.p. 163 °C, ^{13}C NMR (DMSO-d$_6$): 106.2; 94.1; IR (KBr): 1700, 1497, 1444, 1242, 1084, 962 cm^{-1}. Elemental analysis: calcd for C$_4$HI$_4$N: C, 8.40; H, 0; N, 0, found: C, 8.38; H, 0.03; N, 0.10.

Crude TIF was decolorized using activated charcoal in hexane and ethyl acetate as follows: crude TIF (30.0 g) and activated charcoal (4.5 g) were added to a mixture of hexane (500 mL) and ethyl acetate (300 mL) and the final mixture was refluxed overnight. The hot solution was filtered quickly, washed with hot hexane/ethyl acetate (1:1, 100 mL), and then the filtrate was concentrated under reduced pressure recovering the organic solvent which was recycled. The pure TIF was obtained as cream needle crystals (27.2 g, 90.7 % yield).

Tips:

1. If amount of activated charcoal utilized is less than 1.5 g, TIF wasn't decolorized very well and light brown needle crystals were obtained.

2. If ethyl acetate or acetone was used separately for washing the residue without hexane, some impurities may be taken into the filtrate.

The pure (99+%) TIF is a cream color as shown in Figure 2-a and TIF with a small amount of impurities (97+%) usually has a brown color (Figure 2-b) which is contaminated with some unknown black solid.

In this report, we used DSC, TGA and EA to analyze the two different colored TIF materials. The results are summarized in Table 2-1. The DSC and TGA figures are shown in Figure 2-2 to Figure 2-5. In the TGAS curves it is seen that TIF starts to lose weight after it melts which may be because it sublimes after melting melts. The results show that the melting point increases by 0.45 °C when the brown compound was purified to give the cream color, and the decomposition temperature increases 17.77 °C. Elemental analyses of both colored materials match well with the calculated values. TIF is light sensitive.

Figure 2-1°. Pure TIF   Figure 2-1b. Impure TIF

Table 2-1. Properties of TIF

	Pure TIF	Impure TIF
Melting point (°C)	163.19	162.74
Decomposition Point(°C)	289.40	271.63
EA results (Calcd: C 8. 40)	C: 8.46, H: -0.04, N: 0.06	C: 8.63, H: 0.02, N: -0.04

Figure 2-2. DSC of impure TIF.

Figure 2-3. TGA of impure TIF.
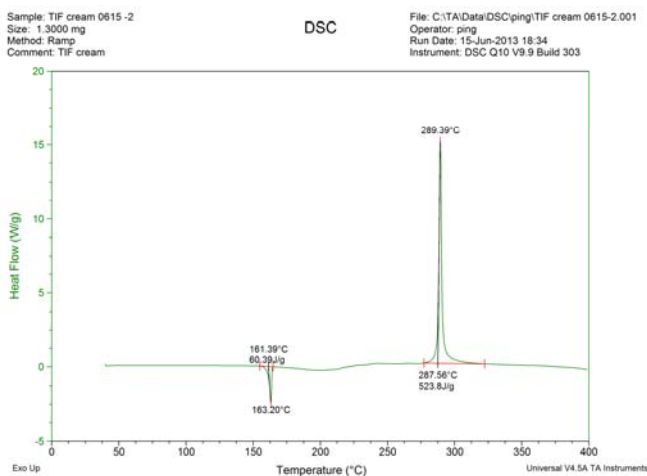
Figure 2-4. DSC of pure TIF.
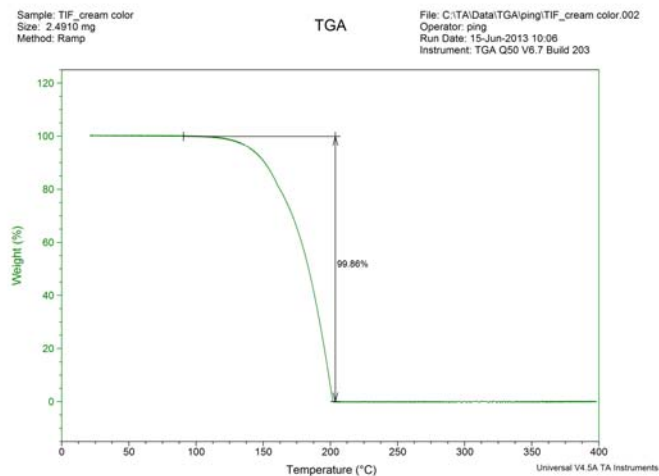
Figure 2-5. TGA of pure TIF.

References
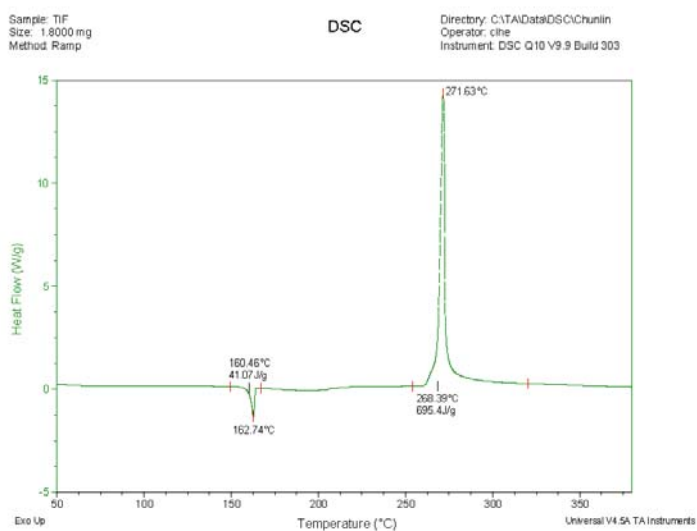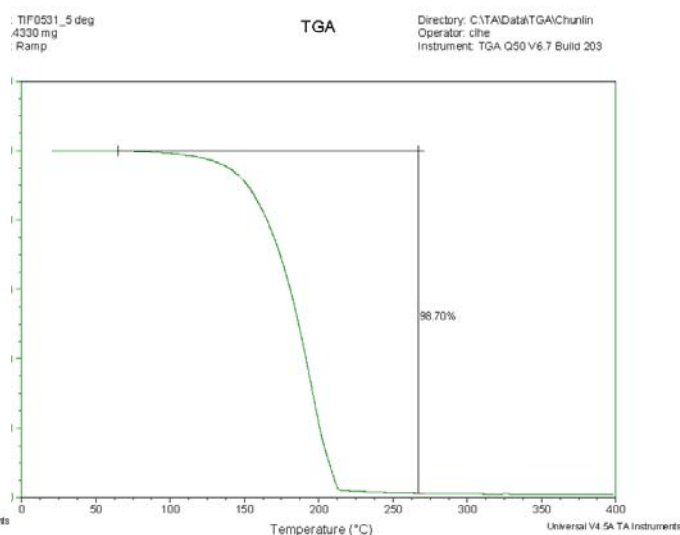1. a) www.bam.de. b) A portion (20 mg) of an iodo compound was subjected to a drop-hammer test using a 5 or 10 kg weight. The range in impact sensitivities according to the UN Recommendations is: insensitive >40 J; less sensitive >=35 J; sensitive >4 J; very sensitive <=3 J.
2. Gaussian 03, Revision D.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, Gomperts, J.; R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. Gaussian, Inc., Wallingford CT, **2004**.
3. Higa, K.; Johnson, C. Private communication to Dr. Su Peiris, and Dr. Jean'ne M. Shreeve, April 19, 2013. Cited with permission from Dr. Curtis Johnson.
4. Ciusa, R., Grilla, G., *Memorias y Revista de la Academia Nacional de Ciencias* **1927**, *46*, 213-222.

ii) Synthesis and characterization of iodoxy compounds

(See Appendix A for full length paper – He, C.; Zhang, J.; Shreeve, J. M. *Chemistry – a European Journal,* **2013**, *19*, 7503-7509

Although explosions of iodoxy compounds have been reported in the literature,[1] those compounds have not been studied as energetic compounds. The densities of 1, 2, 4-triazolium periodate (density, 2.62 g/cm^3) and guanidinium periodate (density, 2.59 g/cm^3) suggest that such oxohalogens may exhibit useful attributes with higher densities than the perchlorates and also exhibit greater effectiveness toward bio-agents. The imidazole and pyrazole-based energetic compounds attract great interest for their good thermal stabilities and sensitivities. We have synthesized several kinds of imidazole or pyrazole-based iodo compounds (Appendix A). Imidazole or pyrazole-based iodoxy compounds can also be of interest for their high densities and thermal stabilities. Therefore, six different iodoxy compounds were synthesized and characterized by IR, and NMR spectra, elemental analysis, and differential scanning calorimetry (DSC). Additionally their detonation properties were calculated and are discussed below.

The most common oxidants that were used for the preparation of iodylarenes from iodoarenes include sodium hypochlorite, sodium periodate, dimethyldioxirane, and Oxone.[2] Since Oxone is a commercially available low cost reagent as well as having

good stability, simple handling and non-toxic nature, it was used for preparing iodoxy compounds using a modified method (Scheme 2 – Appendix A).[2b] For mono iodo (Table 2, entry 3 – Appendix A) compounds, the oxidation can be completed at room temperature using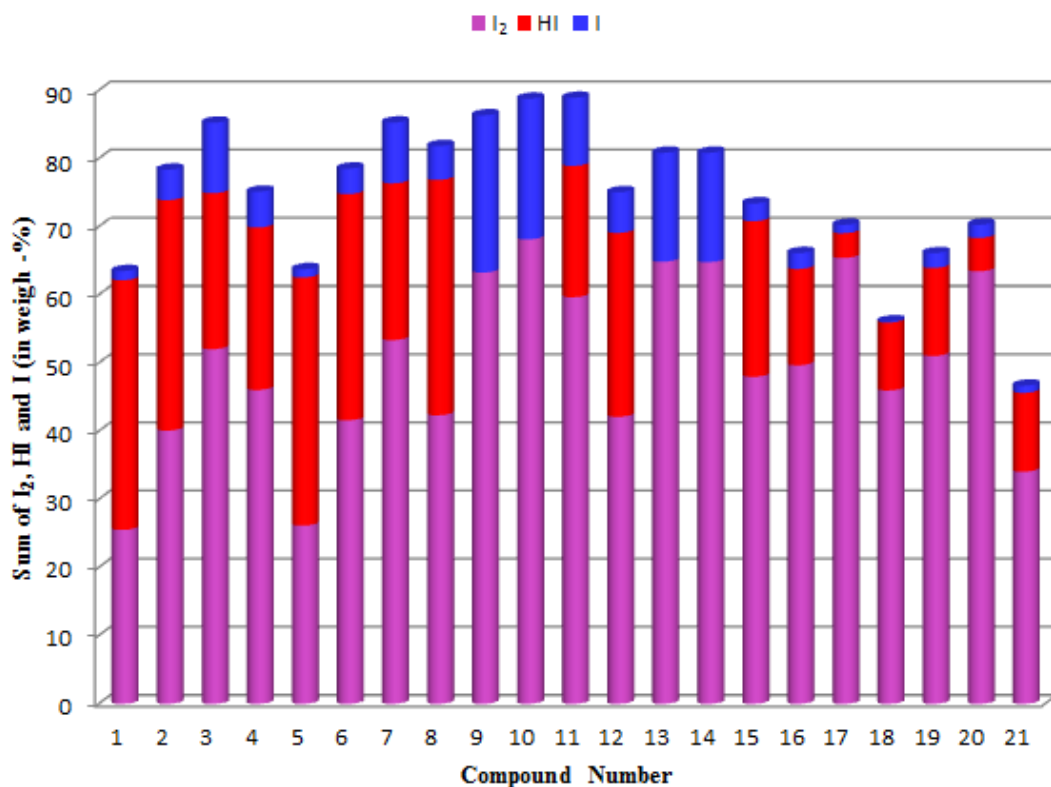 1.3 eq Oxone®. The formation of polyiodo compounds requires heating to 70 °C and extended reaction time was needed to finish the reaction. The N-nitration of imidazole or pyrazole could be achieved under mild conditions using 100% nitric acid and acetic anhydride,[3] while only 100% nitric acid was needed to prepare N-nitro iodoxy compounds in our work. All the compounds were confirmed by elemental analysis. NMR data could not be obtained for 3, 4-di-iodoxypyrazole and 3, 4, 5-triiodoxypyrazole because of their very low solubility in organic solvents.

The impact sensitivities of the iodoxy compounds (Table 2– Appendix A) range between 2 to 40 J. 4,5-Di-iodoxyimidazole hemihydrate (Table 2, entry 1 – Appendix A) shows an unusually low impact insensitivity which may result from the presence of the water in molecule which helps to form extensive hydrogen bonds and improve its impact sensitivity dramatically. The hemihydrate of N-nitro-4-iodoxypyrazole (Table 2, entry 6 – Appendix A) also improves the impact sensitivity to some extent. For pyrazole iodoxy derivatives, the greater number of the iodoxy substituents, the less impact sensitive the compound. The thermal stabilities of the compounds were studied by differential scanning calorimetry (DSC). All iodoxy compounds decomposed between 159 – 227 °C. The 3,4,5-tri-iodoxypyrazole (Table 2, entry 5 – Appendix A) is the least thermally stable while 4,5-di-iodoxyimidazole hemidyrate (Table 2, entry 1 – Appendix A) decomposed at 227 °C. As one of the most important physical properties of energetic compounds, the densities of iodoxy compounds were determined by using a gas pycnometer at 25 °C. The densities range between 2.54 – 3.68 g·cm^{-3}. 4-Iodoxypyrazole (Table 2, entry 3 – Appendix A) has a higher density then diiodoxypyrazole (Table 2, entry 4 – Appendix A) which may arise from the existence of the intramolecular hydrogen bond between O10 and H5 (2.821 Å) based on the optimized structure calculated using the Gaussian 03 suite of programs (Figure 2 – Appendix A).

The heats of formation for iodoxy compounds were calculated by using the Gaussian 03 suite of programs[4] by constructing isodesmic reactions and are summarized in Table 2 – Appendix A). The iodine atoms were optimized via mp2(full)/6-31g(d) at the ECP level, and the heat of formation of CH_3IO_2 was calculated using G2ECP (ZPE=MP2) methodology[5] and for other small molecules were obtained by employing the G2 method.. All the compounds exhibit negative heats of formation except N-nitro-4-iodoxypyrazole which has a positive value of 54.7 kJ/mol. By using the calculated values of the heats of formation and the experimental values for the densities, the detonation velocities (*D*) and detonation pressures (*P*) were calculated using the Cheetah 6.0 program. All the compounds have low detonation pressures range between 10.24 to 28.33 GPa and velocities lie between 4181 to 6897 m/s compared to the traditional energetic compounds but higher than iodo compounds. The detonation properties improve as the number of iodoxy group increases. The N-nitro group enhances the detonation properties markedly but also decreases the density.

The detonation products formed were predicted using Cheetah 6.0 under Chapman-Jouguet conditions and are listed in Table 3 – Appendix A in weight-%. After detonation, most iodine atoms in the molecule are found as I_2, HI and I which are strong biocides. The molecule with more hydrogen atoms forms a high weight percentage of HI. The sum of iodine containing species in weight-% (I_2, HI and I, in gas phase) ranges between 46.7% (**21**) to 88.94% (**11**) as shown in Figure 1 (Figure 4 – Appendix A). The high percentage of these strong biocides in the detonation products makes them promising as potential bio-agent defeat materials.

In summary, six iodoxy compounds were synthesized in moderate yields by using straightforward methods. All the compounds were confirmed by elemental analysis and characterized by IR, ^{1}H and ^{13}C NMR, elemental analysis, and differential scanning calorimetry (DSC). Detonation properties were calculated. The unique high density, high iodine content, and low detonation properties of iodoxy compounds make them interesting in some special energetic fields. The good thermal stability, moderate detonation properties and impact insensitiveness of 4, 5-diiodoxyimidazole hemihydrate makes it a candidate for a low pressure bio-agent additive. <u>This work was terminated during year two.</u>

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iii) Synthesis and characterization of polyiodide compounds

Halogen-containing compounds which can generate strong biocides such as HF, HI or I_2 after decomposition are ideal charges for Agent Defeat Weapons.[1] Polyiodides have attracted a great deal of attention because of their fascinating structural chemistry.[2] Polyiodides have been shown to be very effective against pathogenic organisms in real life situations particularly as chemical agents that are effective in killing, for example, viruses, bacteria and eukaryotic parasites.[3] The N-containing alkyl cations may help to increase the energy and also result in low pressure when cooperating with polyiodide anions. In our continuing interest towards seeking effective materials for bio-agent destruction, polyiodides with various symmetrical alkyl ammonium cations appear to be good candidates.

The iodide salts **1a - 11a** were prepared from the corresponding amine with HI or iodomethane in alcohol or acetonitrile solvent by controlling the stoichiometry of the reaction (Scheme 1). Their properties are given in Table 1 (APPENDIX B). Compounds **2b-5b**, **7b-11b**, and **9c-11c** can be prepared using a straightforward method by heating the iodide salts in appropriate amounts of elemental iodine in ethanolic solution at 50 – 60 °C. After the solvent was evaporated the residue was dried under vacuum at 50 °C overnight to obtain the corresponding polyiodide (Scheme 2).

The physical properties of all iodide and polyiodide compounds are listed in Tables 1 and 2 (Appendix B). Most of iodide compounds have very good thermal stabilities (> 250 °C and the majority >300 °C) except **7a** and **7b** which decomposed at 176.0 and 111.2 °C, respectively. The iodide salts of **1a – 11a** have an iodine content

ranging from 61.29% (**11a**) to 80.34% (**1a**), and the iodine content of the polyiodide salts falls in 82.61% (**11b**) to 90.91% (**2b**). An increase in iodine content destabilizes the corresponding polyiodides (**11a** > **11b** > **11c**).

All the compounds exhibit densities from 1.73 g/cm^3 to 3.33 g/cm^3. The introduction of the polyiodide moiety results in an increase of density from 0.49 g/cm^3 to 1.35 g/cm^3 compared to the corresponding iodide salts; furthermore, the formation of polyiodide also helps to improve the oxygen balance. The impact sensitivity measurements were made using standard BAM techniques; all the compounds were found to be insensitive to impact. The heat of formation for the obtained compounds were calculated by employing the Gaussian 03 (Revision D. 01).[4] The alkyl ammonium cations were obtained by using the G2 method.[5] The iodide, triiodide, pentaiodide and octaiodide anions were calculated using G2ECP method. With the values of the heats of formation and densities, the detonation pressures (P) and velocities (D) were calculated using CHEETAH 6.0 as listed in Tables 1 and 2 (Appendix B).

A suitable crystal for X-ray of **11b** was grown in acetone. Compound **11b** crystallizes in the monoclinic, space group P2$_1$/m. The crystal data and structure refinement details are listed in Table 3 (Appendix B) and the crystal structure is shown in Figure 1.
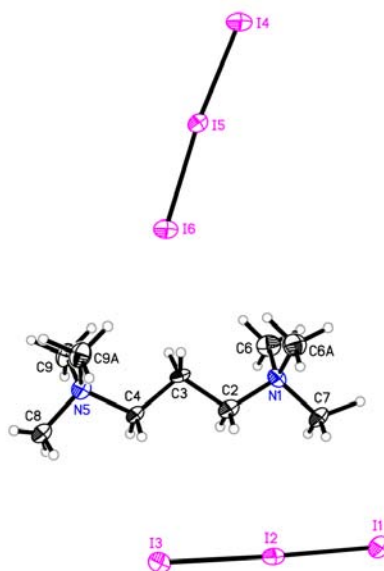
Figure 1. Crystal structure of **11bj**

Synthesis and characterization

The synthesis schemes are shown in Schemes 1 and 2. The synthesis details of all of the iodides and polyiodides can be found in Appendix B.

Alkyl—(NH₂)ₙ + n HI ⟶ Alkyl—(NH₃)ₙ⁺ n I⁻ —n I₂/ EtOH, 60 °C→ Alkyl—(NH₃)ₙ⁺ n I₃⁻

1a-5a **2b-5b**

Alkyl—(NH₂)ₙ =

H₂N—CH₂CH₂—NH₂   H₂N—CH₂CH₂CH₂—NH₂   H₂N—CH₂CH₂—NH—CH₂CH₂—NH₂

1 **2** **3**

H₂N—CH₂CH₂—NH—CH₂CH₂—NH—CH₂CH₂—NH₂   N(CH₂CH₂NH₂)₃   C(CH₂NH₂)₄

4 **5** **6**

Scheme 1. Preparation of alkyl ammonium iodide and triiodide salts

(H₃C)₂N—NH₂ —ClNH₂→ (H₃C)₂N⁺(NH₂)—NH₂ Cl⁻ —KI→ (H₃C)₂N⁺(NH₂)—NH₂ I⁻ —I₂→ (H₃C)₂N⁺(NH₂)—NH₂ I₃⁻

7a **7b**

(H₃C)₂N—NH₂ —CH₃I→ (H₃C)₃N⁺—NH₂ I⁻ —I₂→ (H₃C)₃N⁺—NH₂ I₃⁻

8a **8b**

Alkyl—[N(CH₃)₂]ₙ —n CH₃I / EtOH→ Alkyl—[N(CH₃)₃]ₙ⁺ n I⁻ —n I₂→ Alkyl—[N(CH₃)₃]ₙ⁺ n I₃⁻ —n I₂→

9a - 11a **9b - 11 b**

[Alkyl—[N(CH₃)₃]ₙ⁺ I₈²⁻ **9c-10c**]
[Alkyl—[N(CH₃)₃]ₙ⁺ n I₅⁻] **11c**

Alkyl—[N(CH₃)₂]ₙ =

H₃C—N(CH₃)—CH₂—N(CH₃)—CH₃   H₃C—N(CH₃)—CH₂CH₂—N(CH₃)—CH₃   H₃C—N(CH₃)—CH₂CH₂CH₂—N(CH₃)—CH₃

9 **10** **11**

Scheme 2. Synthesis of quaternary ammonium iodide, triiodide and pentaiodide salts

In summary, during this preliminary work, 11 iodide salts and 11 polyiodide salts were synthesized. Based on measured densities and decomposition temperatures and high iodine content, the polyiodide salts appear to hold major promise as biocidal

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reagents. The thermodynamic data are yet to be calculated, but it appears that the detonation pressures and velocities will be somewhat larger than for TIF but still within a useful low pressure/velocity range. The iodide content is very high. These salts are very attractive candidates!

b) Pentafluorosulfanyl derivatives

i) Pentafluorosulfanyl-substituted poly-1,2,3-triazole compounds

The synthesis and properties determination of dense pentafluorosulfanyl-substituted poly-1,2,3-triazole compounds were undertaken.[1] One sample, 2-(pentafluorosulfanyl-1,2,3-triazol-1-yl)-bis-(N,N-tris(pentafluorosulfanyl-1,2,3-triazol-1-ylethyl)-ethanamine) (**2a**) was submitted to Indian Head for testing for biocidal characteristics. The preliminary results are reported vide infra. <u>However, the decision was made to discontinue study of these pentafluorosulfanyl materials further.</u>

2a
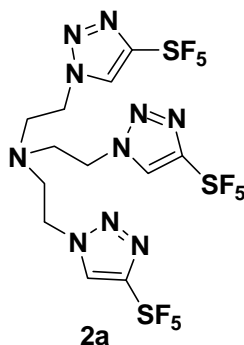
During the first year of the award, **2a** was selected for testing as an explosive. Two and one-half grams of **2a** were submitted to Dr. Jillian Horn at Indian Head for testing which included:
- Perform small scale safety testing.
- Run 'open' air blast test to measure pressure and temperature and reaction/burn time generated.
- Based on results of air blast, decide appropriateness of bug-kill test, and if so, which one.

The following information had been provided by Indian Head.
- 141 cm impact (low sensitivity)
- 180 psig friction (low sensitivity)
- 0.165 Joules ESD (medium sensitivity)

Based on these data and the very competitive performance obtained for tetraiodo furan (vide infra), it was decided no further tests were to be carried out. This pentafluorosulfanyl compound effort was terminated during the second year.

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YEAR III

iii) Accomplished under these goals

Good progress has continued to be made toward meeting the objective of this work. Our synthetic routes are reasonably straightforward and we utilize Gaussian 03 methodology to estimate enthalpy of formation; after determining the experimental density with a gas pycnometer, detonation properties (pressure and velocity) were calculated using Explo5 6.01 or Cheetah 6 or 7. Three families of compounds have been prepared, viz., i) polyiodoheterocycles; ii) polyiodides; and iii) polyiodoheterocyclic iodides, iodates and octaoxotriiodates. The compounds have been carefully characterized via ^{1}H, and ^{13}C (and sometimes ^{15}N) NMR and infrared spectral analysis, DSC (thermal stability), elemental analysis, and impact sensitivity. In keeping with the terms of the award, a subcontract was established with Indian Head to test compounds for their efficacy as biocidal reagents. Based on the results obtained from preliminary testing tetraiodo furan at Indian Head, the latter was down selected for formulation studies which were initially carried out at China Lake. The results are very encouraging. DTRA (Dr. Suhithi Peiris) outsourced the synthesis of six kilos of TIF to Galaxy Chemicals (Tulsa, OK) to enable further study of the compound (transitioned to 6.2) at Indian Head and Elgin. The Idaho group spent a consider amount of time working with Galaxy Chemicals in the first stages of delivering the six kilos.

a) Iodine-containing compounds

i) Polyiodoheterocycles

Continuing efforts to enhance the synthesis and purification of TIF.

Work with TIF (tetraiodofuran) has been ongoing particularly in the effort to develop a more suitable route to the compound and to establish a purification method which is straightforward and rewarding.

Work at Indian Head

During this past year (FY 2014), 100 grams of pure TIF were shipped to Dr. Jim Lightstone at Indian Head for biocidal testing. These tests went very well. A call for six kilos of TIF was outsourced by Dr. Suhithi Peiris. This has now been delivered to Indian Head and further testing is ongoing. No report has been received from them telling of progress.

TIF and its properties.

Synthetic procedure currently in use

Tetraiodofuran:[4] Yield: 52%. M.p. 163 °C, ^{13}C NMR (DMSO-d_6): 106.2; 94.1; IR (KBr): 1700, 1497, 1444, 1242, 1084, 962 cm^{-1}. Elemental analysis: calcd for C_4HI_4N: C, 8.40; H, 0; N, 0, found: C, 8.38; H, 0.03; N, 0.10.

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Tips:
1. If amount of activated charcoal utilized is less than 1.5 g, TIF wasn't decolorized very well and light brown needle crystals were obtained.
2. If ethyl acetate or acetone was used separately for washing the residue without hexane, some impurities may be taken into the filtrate.
The pure (99+%) TIF is a cream color and TIF with a small amount of impurities (97+%) usually has a brown color which is contaminated with some unknown black solid. In this report, we used DSC, TGA and EA to analyze the two different colored TIF materials. The results are summarized in Table 1. The results show that the melting point increases by 0.45 °C when the brown compound was purified to give the cream color, and the decomposition temperature increases 17.77 °C. Elemental analyses of both colored materials match well with the calculated values. TIF is light sensitive.

Table 1. Properties of TIF

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Alternate routes to TIF -   Tetraiodofuran (TIF) revisited

      Since tetraidofuran (TIF) has been demonstrated to be a promising biocide in recent tests both at China Lake and Indian Head, the need for larger amounts of the material has become a requirement. Unfortunately the current, and only known, route to TIF is not very satisfactory for producing the compound in large amounts. TIF was prepared in three steps in an old fashioned method (vide supra),[1] and the process utilizes mercuric acetate which is very toxic and expensive. An improved straightforward method for the synthesis of TIF is necessary, especially when it is needed to be synthesized on a large scale. We were continuing to seek new, effective methods to synthesize this material. To date we have met with little success in generating such methods. However, we will continue to attempt to develop methodologies which permit production of TIF in a more straightforward and more environmentally benign manner (without mercury intermediates – vide infra). Several routes that appeared to hold some possibility of success were:

      a) The iodination method described in Scheme 1 has been successfully used in preparing 2,3,4,5-tetraiodothiophene.[2] However, in case of the iodination of furan, the same conditions and also sealed conditions at 0 °C or reflux conditions were tried, but no trace of iodination products was found.
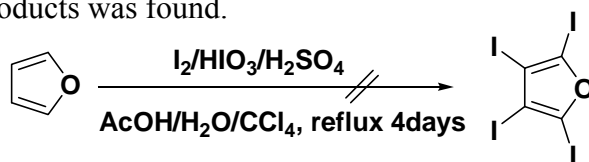
Scheme 1

      b) Although the method in Scheme 2 was used to prepare hexaiodobenzene,[3] the same conditions failed in the case of the reaction with furan; furan was recovered unscathed after reaction according to the ^{1}H NMR.
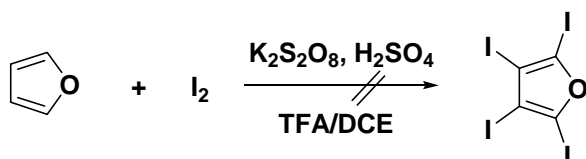
Scheme 2

c) The method in Scheme 3 was described in the preparation of tetraiodopyrrole.[4] In the attempt to prepare TIF using the same conditions, trace amounts of a mixture of mono and diiodofuran, and large amounts of unreacted furan were observed in the ^{1}H NMR.
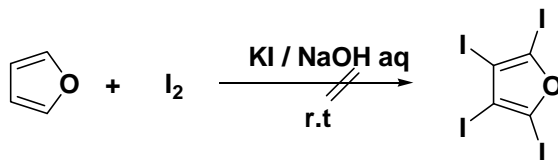
Scheme 3

d) The iodine monochloride pyridine complex is an efficient iodination reagent for aromatic compounds.[5] A mixture of furan and monoiodofuran in Scheme 4 was observed in the MS spectrum when the conditions were applied to the reaction with furan but no TIF!
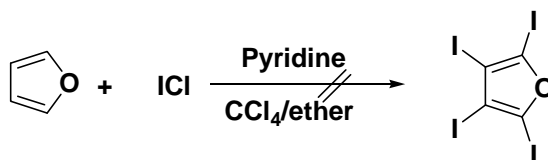
Scheme 4

e) The mixture of iodine and 30% H_2O_2 in Scheme 5 was found to be a green iodinating reagent.[6] However, monoiodofuran in low yield was found in the MS spectrum after the reaction with furan under the same conditions. Thus, the original methodology
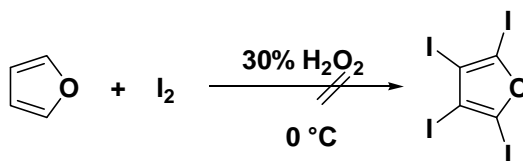
Scheme 5

appears to be superior to any of the different routes that were tried in an effort to play a significant, and higher yield role while concomitantly being less environmentally hazardous. The search for a more lucrative route will be continued.

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ii) Alkyl ammonium cation stabilized biocidal polyiodides with adaptable high density and low pressure.

(See Appendix C for full length paper – He, C.; Parrish, D. A.; Shreeve, J. M. *Chemistry – a European Journal,* **2014**, *20*, 6699-6706.

The effective application of biocidal species requires building the active moiety into a molecular back bone that can be delivered and decomposed on demand under conditions of low pressure and prolonged high temperature detonation. The goal is to destroy storage facilities and their contents while utilizing the biocidal products arising from the released energy to destroy any remaining harmful airborne agents. Decomposition of carefully selected iodine-rich compounds can produce large amounts of the very active biocides, hydroiodic acid (HI) and iodine (I_2). Polyiodide anions, viz., I_3^-, I_5^-, which are excellent sources of such biocides, can be stabilized through interactions with large, symmetric cations such as alkyl ammonium salts. We have designed and synthesized suitable compounds of adaptable high density up to 3.33 g/cm^3, that are low pressure polyiodides with various alkyl ammonium cations whose deliverable iodine contents range between 58.0–90.9%. The N-containing alkyl cations may help to increase the energy and also result in low pressure when cooperating with polyiodide anions. In our continuing interest towards seeking effective materials for bio-agent destruction, polyiodides with various symmetrical alkyl ammonium cations appear to be good candidates.

The iodide salts **1a - 11a** were prepared from the corresponding amine with HI or iodomethane in alcohol or acetonitrile solvent by controlling the stoichiometry of the reaction (Scheme 1). Their properties are given in Table 1 (Appendix C). Compounds **2b-5b**, **7b-11b**, and **9c-11c** can be prepared using a straightforward method by heating the iodide salts in appropriate amounts of elemental iodine in ethanolic solution at 50 – 60 °C. After the solvent was evaporated the residue was dried under vacuum at 50 °C overnight to obtain the corresponding polyiodide (Scheme 2).

The physical properties of all iodide and polyiodide compounds are listed in Tables 1 and 2 (Appendix C). Most of iodide compounds have very good thermal stabilities (> 250 °C and the majority >300 °C) except **7a** and **7b** which decomposed at 176.0 and 111.2 °C, respectively. The iodide salts of **1a – 11a** have an iodine content ranging from 61.29% (**11a**) to 80.34% (**1a**), and the iodine content of the polyiodide salts falls in 82.61% (**11b**) to 90.91% (**2b**). An increase in iodine content destabilizes the corresponding polyiodides (**11a** > **11b** > **11c**).

All the compounds exhibit densities between 1.73 g/cm^3 to 3.33 g/cm^3. The introduction of the polyiodide moiety results in an increase of density from 0.49 g/cm^3 to 1.35 g/cm^3 compared to the corresponding iodide salts; furthermore, the formation of polyiodide also helps to improve the oxygen balance. The impact sensitivity measurements were made using standard BAM techniques; all the compounds were found to be insensitive to impact. The heat of formation for the obtained compounds were calculated by employing the Gaussian 03 (Revision D. 01).[4] The alkyl ammonium cations were obtained by using the G2 method.[5] The iodide, triiodide, pentaiodide, and octaiodide anions were calculated using G2ECP method. With the values of the heats of formation and densities, the detonation pressures (P) and velocities (D) were calculated using CHEETAH 6.0 (Dr Joseph Hooper, Naval Postgraduate School, Monterey, CA 93943) as listed in Tables 1 and 2 (Appendix C).

A suitable crystal for X-ray of **11b** was grown in acetone. Compound **11b** crystallizes in the monoclinic, space group P2$_1$/m. The crystal data and structure refinement details are listed in Table 3 (Appendix C) and the crystal structure is shown in Figure 1.
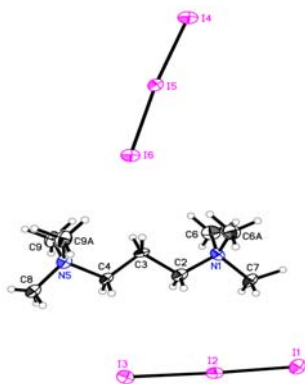
Figure 1. Crystal structure of **11b**

Synthesis and characterization

The synthesis schemes are shown in Schemes 1 and 2.

37
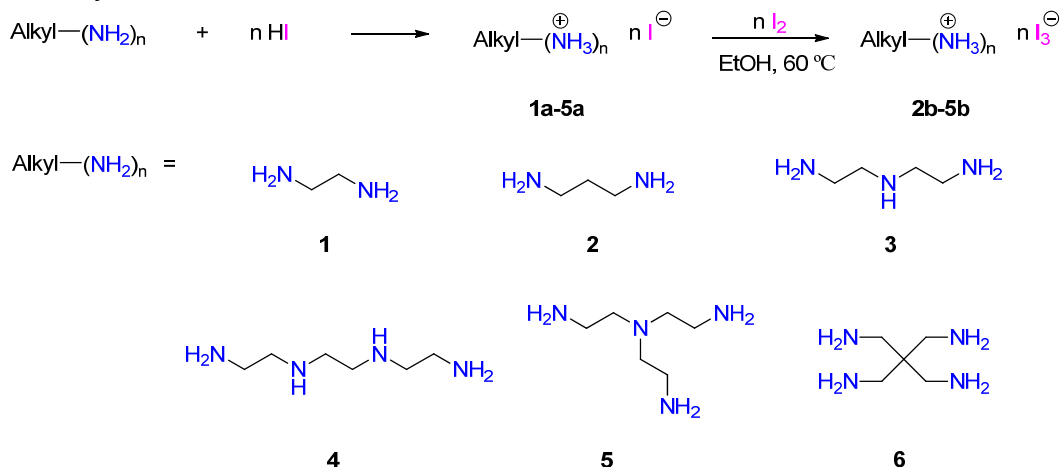
Scheme 1. Preparation of alkyl ammonium iodide and triiodide salts.
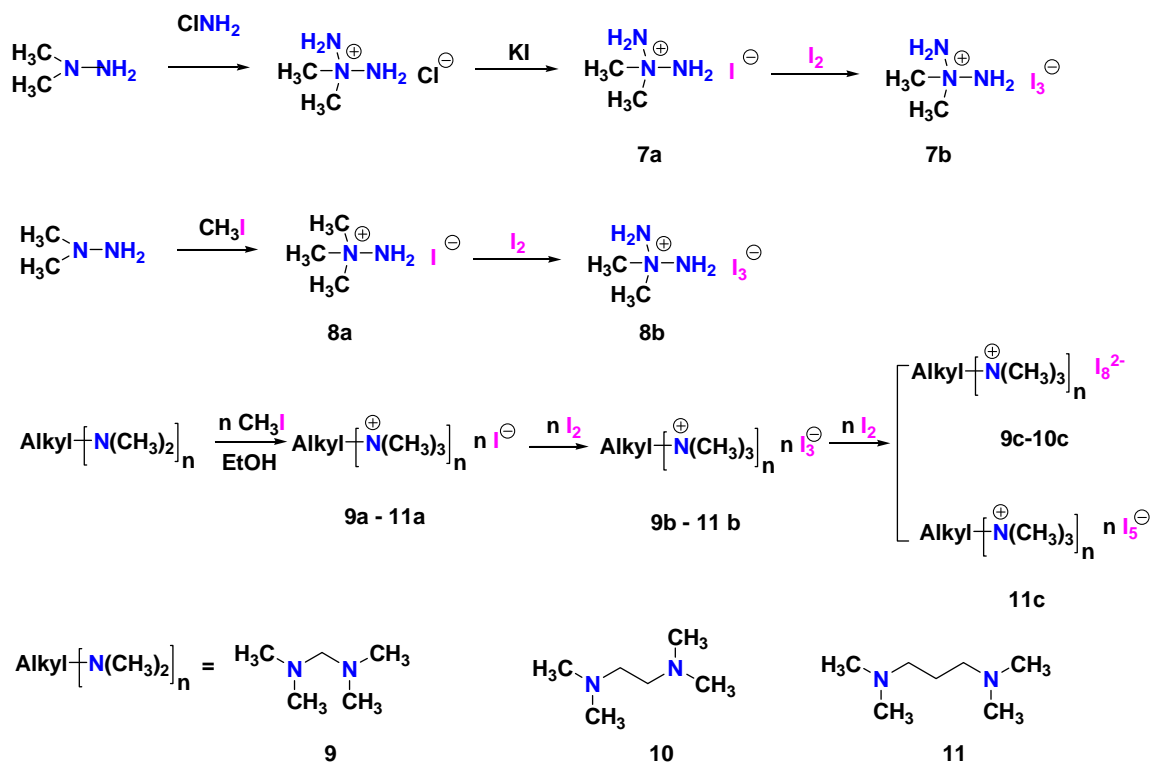
Scheme 2. Synthesis of quaternary ammonium iodide, triiodide and pentaiodide salts.

The synthesis details of all of the iodides and polyiodides can be found in Appendix C.

In summary, during this preliminary work, 11 iodide salts and 11 polyiodide salts were synthesized. Based on measured densities and decomposition temperatures and high iodine content, the polyiodide salts appear to hold major promise as biocidal reagents. The thermodynamic data are yet to be calculated, but it appears that the detonation pressures and velocities will be somewhat larger than for TIF but still within a useful low pressure/velocity range. The iodide content is very high. These salts are very attractive candidates!

As part of the subcontract agreement with Dr. James Lightstone at Indian Head, 20 grams of compound **11c** were submitted for preliminary testing. Apparently interest was lost since no information was received.
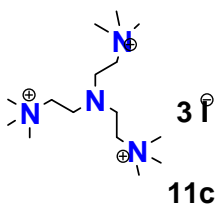
11c

iii) Polyiodoheterocyclic iodides, iodates and octaoxotriiodates

The current formulations to generate the species of I, HI and /or I_2 often contain aluminum, iodine-rich compounds (fuels) and HI_3O_8 or a salt as an extra oxidizer. Therefore, if it is possible to form a salt with an iodine-rich cation and $I_3O_8^-$ or other oxidizing anion, it will have the advantage of being a fuel with a built-in oxidizer, as well as decreasing the solid residue after the decomposition.

Previously, we reported a few iodine-rich neutral compounds,[1] e.g., 1-methyl-2,4,5-triiodoimidazole (**1**) has a relatively high iodine content of 82.8%. Many quaternized imidazolium cations were reported in the field of ionic liquids. Here, we have quaternized **1** by reacting it with excess CH_3I in DMF at 50 °C for 4h (Scheme 1); however, a mixture of 1,3-dimethyl-2,4,5-triiodoimidazolium iodide (**2**) and 1,3-dimethyl-4,5-diiodoimidazolium iodide (**3**) were precipitated from the reaction mixture in a ratio of 4:1 based on the ^{1}H NMR spectrum. Both compounds **2** and **3** have poor solubility in most of organic solvents as well as water, so it is difficult to isolate them. Pure **3** can be prepared by the quaternization of 4,5-diiodoimidazole under similar reaction conditions with excess CH_3I (Scheme 2).
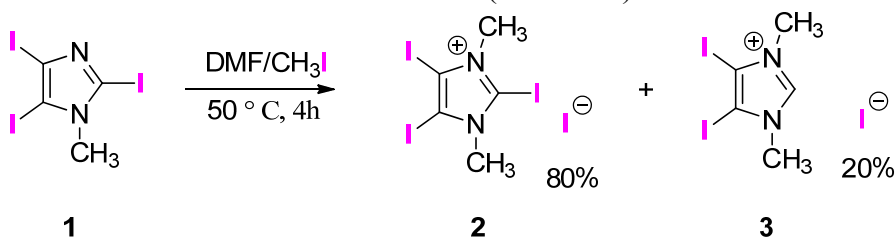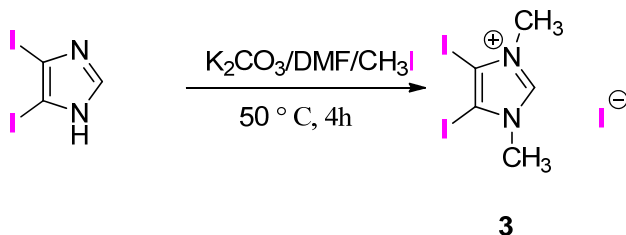
Scheme 1 Quaternization of **1**

Scheme 2 Quaternization of 4,5–diiodoimidazole

The methylene and ethylene bridged 4,5-diiodoimidazole **4** and **5** were prepared by reacting 4,5-diiodoimidazole with KOH and diiodomethane or 1,2-dibromoethane in DMF in the presence of a phase transfer catalyst (tetraethylammonium bromide) according to a modified method described in the literature.[2] The quaternization of **4** and **5** to form salts **6** and **7** were performed using a similar methodology as for compound **3** (Scheme 3). The methylene and ethylene bridged 2,4,5-triiodoimidazole **8** and **9** were prepared in the same manner. Quaternization is still underway (Scheme 4).
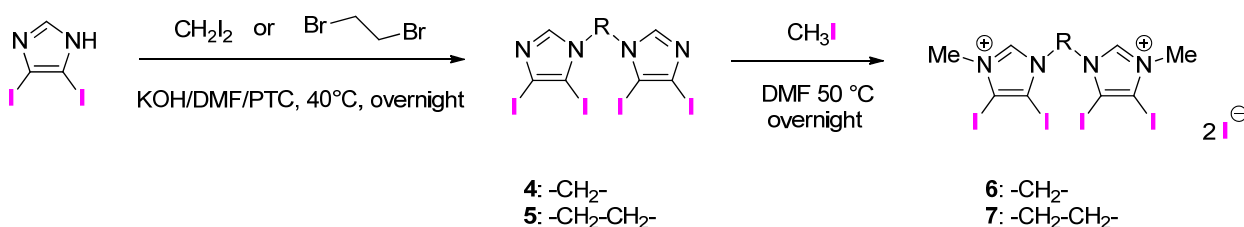
Scheme 3 The Preparation and quaternization of methylene and ethylene bridged 4,5-diiodoimidazoles.
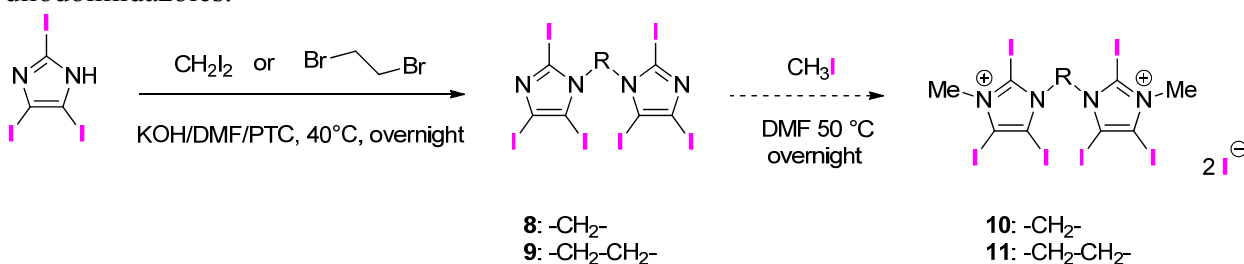
Scheme 4 Preparation and quaternization of methylene and ethylene bridged 2,4,5-triiodoimidazoles.

With these iodide salts, we are now intending to introduce oxidizing anions such as IO_3^-, IO_4^- or $I_3O_8^-$ via metathesis reactions with the corresponding silver salts. $AgIO_3$ and $AgIO_4$ were prepared by reaction of $AgNO_3$ with $NaIO_3$ and $NaIO_4$, respectively. AgI_3O_8 was prepared according to the literature method.[3] While all the iodides have poor solubility in water, the iodates salts have good water solubility. The pure iodate salts can be collected by filtration to remove the insoluble AgI, and the water evaporated. This work is continuing as year III ended.

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YEAR IV

iii) Accomplished under these goals

Good progress has continued to be made toward meeting the objective of this work. Our synthetic routes are reasonably straightforward and we utilize Gaussian 03 methodology to estimate enthalpy of formation; after determining the experimental density with a gas pycnometer, detonation properties (pressure and velocity) were calculated using Explo5 6.01 or Cheetah 6 or 7. Two families of compounds have been prepared, viz., i) polyiodoheterocycles; and ii) polyiodoheterocyclic iodides, iodates and octaoxotriiodates. The compounds have been carefully characterized via ^{1}H, and ^{13}C (and sometimes ^{15}N) NMR and infrared spectral analysis, DSC (thermal stability), elemental analysis, and impact sensitivity.

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a) Iodine-containing compounds

i) Polyiodoheterocycles

a) Polyiodopyrazoles

Various periodo heterocyclic arenes including tetraiodofuran (TIF) and 3, 4, 5-triiodopyrazole have been synthesized in our lab and studied systematically (Figure 1).[1a] They are being tested as effective antibioagent ingredients suitable for application as ADWs. Polyiodide salts which have low vapor pressure, high densities, and high iodine content also provide another opportunity to increase the iodine concentration in target compounds.[1b]
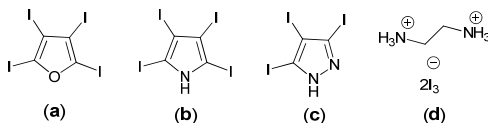
Figure 1: Possible ADWs - (a) Tetraiodofuran (TIF); (b) 2,3,4,5-Tetraiodo-1H pyrrole; (c) 3,4,5-Triiodo-1H-pyrazole; (d) Ethane-1,2-diammonium-bis(triiodide).

Current methods for the iodination of pyrazoles suffer from a variety of difficulties. Pyrazoles with electron donating substituents have been iodinated using iodine-iodide (I_2-KI) or iodine monochloride (ICl); both routes often use large quantities of reactants.[2] An iodine-aqueous ammonia combination gives a mixture of 3, 4-diiodo- and 3, 4, 5-triiodopyrazoles in very low yields.[3] Only diiodo derivatives were obtained when an oxidative iodination methodology – I_2-HIO$_3$ – was attempted.[4] Likely because of the lack of good synthetic routes, the chemistry and properties of polyiodopyrazoles have not been studied widely.

Now we report an efficient synthesis route for polyiodopyrazoles, viz., 3, 4, 5-triiodopyrazole (1), 1-methyl-3, 4, 5-triiodopyrazole (2) and 1-diiodomethyl-3, 4, 5-triiodopyrazole (3) in good to excellent yields. The introduction of the diiodomethyl group is an effective way to increase iodine concentration. Nitration of 1 and 2 leads to the formation of the previously inaccessible 3, 4-dinitro-5-iodopyrazole (4) and 1-methyl-3, 4-dinitro-5-iodopyrazole (5), respectively, giving rise to more energetic iodopyrazoles.

Our continuing interest in ADWs, led us to seek alternative and more lucrative routes to the synthesis of polyiodopyrazoles. Thus a recent report where it was possible to synthesize various polyiodobenzenes by employing molecular iodine under electrophilic conditions, appeared to be useful,[5] although the analytical purity of the products was not established using elemental analysis. Potassium persulfate was used as an oxidant in the presence of trifluoroacetic and sulfuric acids to generate the electrophilic species, I^+. It is likely that only highly stable substrates could survive under these harsh conditions thus suggesting pyrazoles known for their stability as excellent candidates for electrophilic substitution reactions.

Three equivalents of pyrazole or 1-methylpyrazole were treated with two equivalents of iodine in the presence of equal amounts of potassium persulfate in dichloroethane to obtain 3, 4, 5-triiodopyrazole (1) or 1-methyl-3, 4, 5-

triiodopyrazole (**2**) in 63% and 82% yields, respectively. Compounds **1** and **2** were characterized by NMR, and IR spectra, elemental analysis, and DSC measurements (Scheme 1). The carbon-bonded methylene group in acetic acid is considered to be an active group for electrophilic nitration; it can be converted into the trinitromethyl group under nitrating conditions. The 1-acetic acid substituent in pyrazole has a 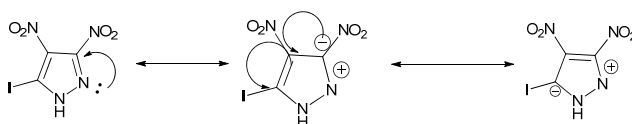similar active methylene group, and although it seemed likely that it should be possible to generate the triiodomethyl moiety using electrophilic iodination, only 1-diiodomethyl-3, 4, 5-triiodopyrazole (**3**) was obtained in 30% yield (Scheme 1). It was fully characterized by using NMR, and IR spectra, elemental analysis, and DSC measurement techniques. Similar reactions with other heterocycles which contained the methylene group of acetic acid failed to react. However, apparently the nitrogen-linked acetic acid group has a sufficiently active methylene group for successful electrophilic iodination reactions under present conditions. After discovering a reliable synthetic route to 3, 4, 5 triiodopyrazole, attempts were made to introduce nitro groups onto the pyrazole ring.
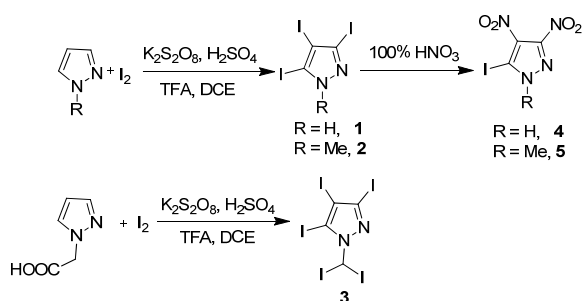
Scheme 1: Synthesis of **1-5**

Although a variety of nitrating conditions were tried, it was not possible to obtain the 3, 4, 5-substituted trinitropyrazole. However, nitration of 3, 4, 5-triiodopyrazole (**1**) or 1-methyl-3, 4, 5-triiodopyrazole (**2**) with 100% nitric acid gave the new 3, 4-dinitro-5-iodopyrazole (**4**) or 1-methyl-3, 4-dinitro-5-iodopyrazole (**5**), respectively (Scheme 1), both of which previously had been inaccessible. Each was characterized by NMR, and IR spectra, elemental analysis and DSC measurement techniques. Single crystal structure analysis was carried out for **5**. Although **4** and **5** appeared to be susceptible to nucleophilic attack, e,g., to replace iodo at the 5-position, neither amination nor azidation of **4** and **5** under varying conditions was successful. This may arise from significant localization of a negative charge at position 5 in the ring thus enhancing the strength of the carbon-iodine bond and precluding substitution (Scheme 2).

Scheme 2: Delocalization of electrons in **4**

The structure of **5** was obtained by X-ray single crystal crystallography. The crystallographic data are summarized in the Electronic Supporting Information. Suitable crystals were obtained by the slow evaporation of a solution of **5** in benzene and diethyl ether. The crystals are triclinic falling in the $P2_1$ space group with two molecules per

crystal lattice (Figure 4). The bond length between N1 and N2 is 1.364(6) Å falling in the typical range of N–N single bonds (1.363(11)–1.366(12) Å).[6a] The distance between the C(4) ring carbon and nitrogen of the nitro group bonded to C(4) – N(8) is 1.419(8) Å. Similarly, the C(5) –N(11) bond length in 3, 4, 5-trinitropyrazole is 1.4538 (14) Å.[7] Thus the effect of iodine substituents is clearly seen in shortening of the C(4)-N(8) bond and lengthening of the C(5)-N(11) bond in comparison to similar bonds in 3, 4, 5-trinitropyrazole. The carbon-iodine bond length for C(3)-I(7) is 2.039(5) Å which is shorter than the normal carbon-iodine single bond length, 2.13 Å. [6]The shorter bond length may account for the failure of the amination or azidation reactions of **5.**

Figure 4: (a) Thermal ellipsoid plot (50%) of **5**. Hydrogen atoms are included but are unlabeled for clarity. (b) Ball and stack packing diagram of **5** viewed down the a-axis.

Polyiodopyrazoles, 3, 4, 5-triiodopyrazole (**1**), 1-methyl-3, 4, 5-triiodopyrazole (**2**) and N-diiodomethyl-3, 4, 5-triiodopyrazole (**3**), were synthesized in efficient electrophilic reactions using molecular iodine in the presence of trifluoroacetic and sulfuric acid; the calculated detonation properties and products suggest that the compounds may be effective bio agent defeat agents. A synthetic method was developed as an effective strategy for introducing an N-diiodomethyl group into pyrazole. Nitration of **1** and **2** with 100% HNO_3 resulted in the formation of the heretofore inaccessible iodo dinitropyrazoles, **4** and **5**. These polyiodopyrazoles may have application not only as ADWs but also in other areas such as medicinal chemistry, materials science, and synthetic organic chemistry.

[1] (a) He, C.; Zhang, J.; Shreeve, J. M. *Chem. Eur. J.* **2013**, *19*, 7503-7509; (b) He, C.; Parrish, D. A.; Shreeve*, J. M. Chem. Eur. J.* **2014**, *20*, 6699 – 6706

[2] (a) Hüttel, R.; Schäfer, O.; Jochum, P. *Liebigs Ann. Chem.* **1955**, *593*, 200–207. (b) Hansen, J. F.; Kim, Y. I.; Griswold, L. J.; Hoelle, G. W.; Taylor, D. L.; Vietti, D. E.; *J. Org. Chem.* **1980**, *45*, 76–80. (c) Holzer, W.; Gruber, H. *J. Heterocycl. Chem.* **1995**, *32*, 1351–1354.

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[5] (a) Rahman, M. A.; Shito, F.; Kitamura, T. *Synthesis* **2010**, 27-29. (b) Rozen, S.; Zamir, D.; *J. Org. Chem.* **1990**, *55*, 3552-3555.

[6] (a) Zhang, Q.; Zhang, J.; Parrish, D. A.; Shreeve, J. M. *Chem. Eur. J.* **2013**, *19*, 11000-11006. (b). Hervé, G.; Roussel, C.; Graindorge, H. *Angew. Chem.* **2010**, *122*, 3245-3249*; Angew. Chem. Int. Ed*. **2010**, *49*, 3177-3181.

[7] http://cccbdb.nist.gov/2008.

ii) Versatile polyiodopyrazoles: synthesis and biocidal promise
(See Appendix D for full length paper – Chand, D.; Shreeve, J. M. *Chem. Commun.* **2015**, *51*, 3438-3441)

iii) Polyiodoheterocyclic iodides, iodates and octaoxotriiodates

a) Iodine-rich salts with oxyanions

As the Third Annual Report was being finalized in June 2014, we had initiated this study so there is some repetition below but over the time of this reporting period, we have made good progress toward our goal of preparing salts with iodine-rich cations and oxygen-containing anions.

The current formulations to generate the species of I, HI and /or I_2 always contain aluminum, iodine-rich compounds (fuels) and HI_3O_8 or $Bi(I_3O_8)$ as an extra oxidizer. Therefore, if we build a salt with iodine-rich cation and $I_3O_8^-$ or other oxidizing anions, it will have the advantage of reducing the amount of external oxidizer or without using an extra oxidizer, as well as decrease the solid residue after the decomposition.

We have reported a few iodine-rich neutral compounds during the past few years,[1] including 1-methyl-2,4,5-triiodoimidazole (**1**) that has a relative high iodine content of 82.8%. A large number of quaternized imidazolium cations were reported in the fields of ionic liquids. Herein, we tried to quaternize **1** by reacting with excess CH_3I in DMF at 50 °C for 4h (Scheme 1), however, a mixture of 1,3-dimethyl-2,4,5-triiodoimidazolium iodide (**2**) and 1,3-dimethyl-4,5-diiodoimidazolium iodide (**3**) were precipitated from the reaction mixture in a ratio of 80: 20 based on the ${}^1H$ NMR spectrum. Both **2** and **3** have poor solubility in most organic solvents as well as water, so it is difficult to isolate them. Pure **3** can be prepared by the quaternization of 4,5-diiodoimidazole in similar reaction conditions with excess CH_3I (Scheme 2).
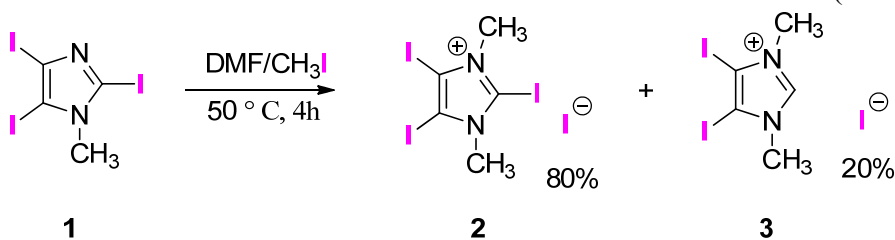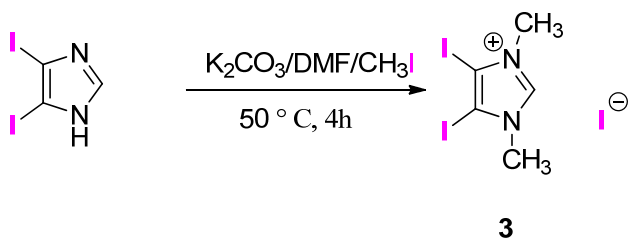
Scheme 1 Quaternization of **1**.

Scheme 2 Quaternization of 4,5-diiodoimidazole.

The methylene and ethylene bridged 4,5-diiodoimidazole, **4** and **5,** were prepared by reacting 4,5-diiodoimidazole with KOH and diiodomethane or 1,2-dibromoethane in DMF using a phase transfer catalyst tetraethylammonium bromide, according to a modified method described in the literature.[2] The quaternization of **4** and **5** leads to the formation of salts **6** and **7** was performed using a way similar to that for preparing compound **3** (Scheme 3). Instead of reacting with methyl iodide to form the cation, the reactions of 4, 5 or 4,5-diiodoimidazoles with tosyl hydroxylamine generates the cations with the N-NH$_2$ group which could improve the oxygen balances of the products (Scheme 4).
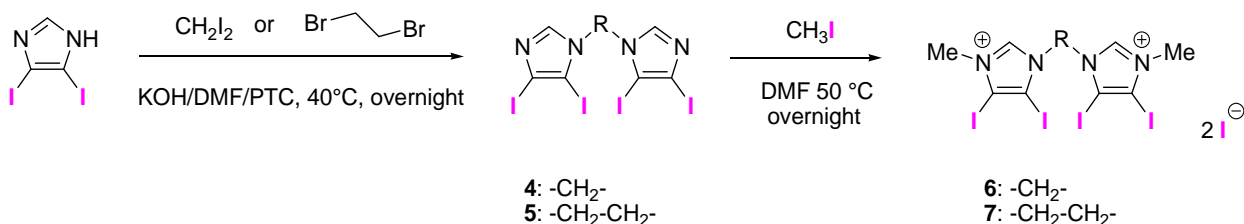
Scheme 3 Preparation and quaternization of methylene and ethylene bridged 4,5-diiodoimidazoles.
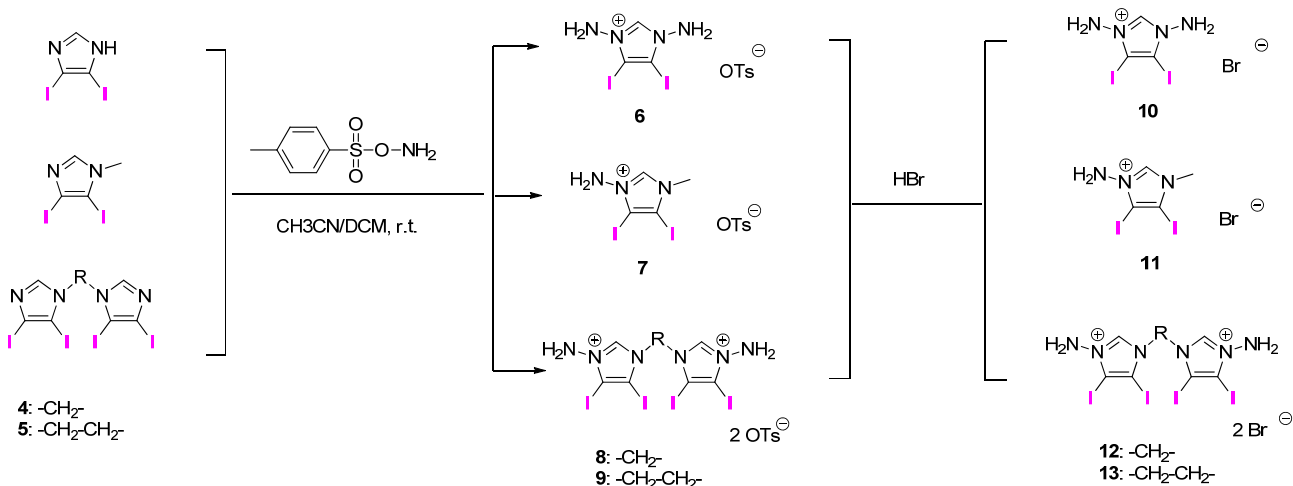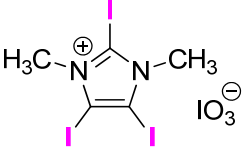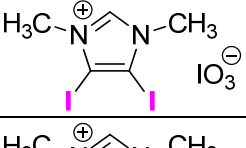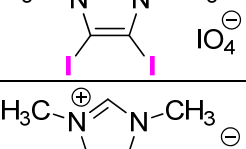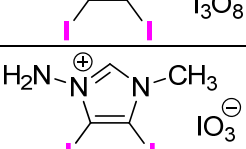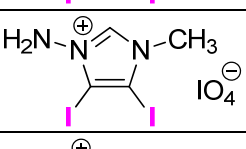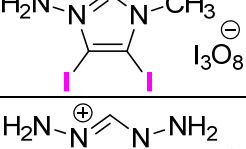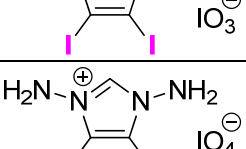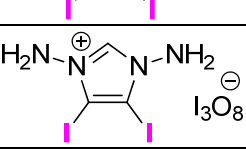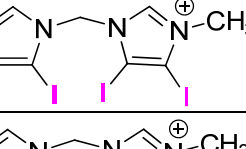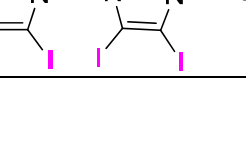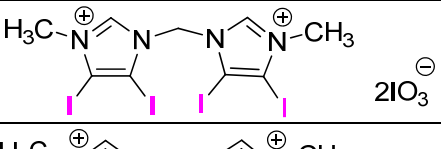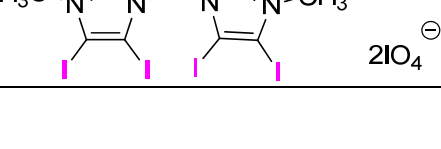
Scheme 4 Preparation of cations by amination.
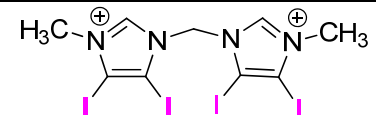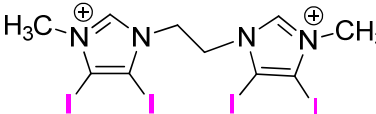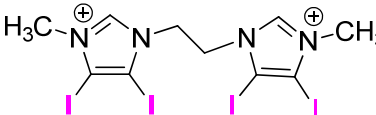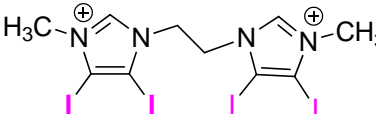
With all the iodide or bromide salts in hand, we introduced the oxidizing anions such as IO_3^-, IO_4^- or $I_3O_8^-$ via metathesis reaction with the corresponding silver salts (Scheme 5). The $AgIO_3$, and $AgIO_4$ were prepared by reacting $AgNO_3$ with $NaIO_3$ and $NaIO_4$, respectively. AgI_3O_8 was prepared according to the literature.[3] While the iodides have poor solubility in water, the iodate salts have good solubility. The pure iodate salts can be collected by filtration to remove the insoluble AgI, and removing the water from the filtrate. In the case of salt **14**, a mixture of **2** and **3** (80:20) was used, the product obtained by evaporating the water in the filtrate was washed with small amounts of water, air dried to obtain salt **14** which is pure enough to achieve good elemental analyses.
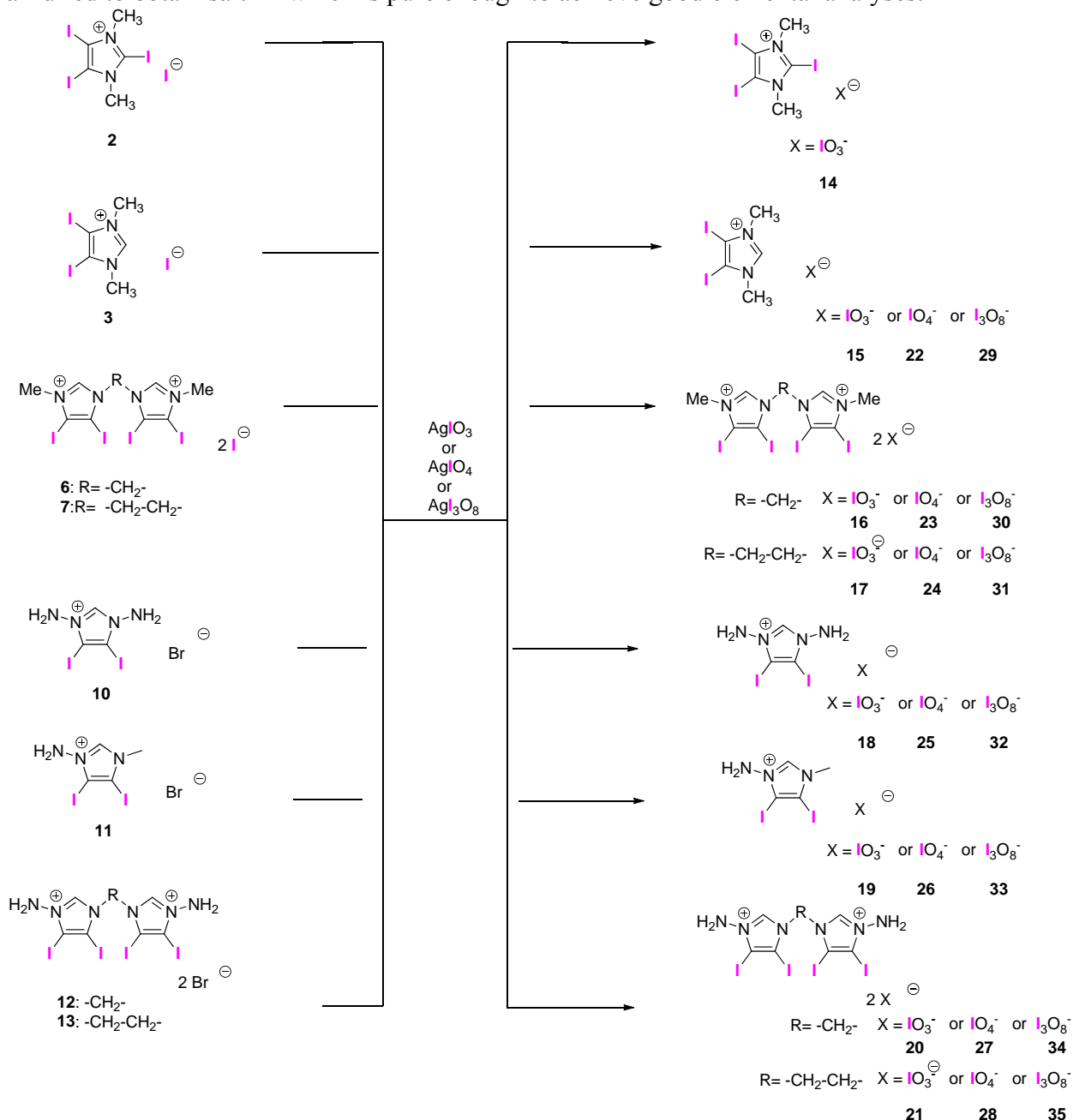
Scheme 5 Preparation of salts with IO_3^-, IO_4^- or $I_3O_8^-$ anions via metathesis reactions.

Characterization

Compound	Structure	DSC	1H NMR	13C NMR	EA
1	H_3C–N$^+$/N–CH_3 imidazolium, IO_3^-	177.4	√	√	√
2	H_3C–N$^+$/N–CH_3 imidazolium, IO_3^-	186.1	√	√	√
3	H_3C–N$^+$/N–CH_3 imidazolium, IO_4^-	135.7	√	√	√
4	H_3C–N$^+$/N–CH_3 imidazolium, $I_3O_8^-$	178.1	√	√	
5	H_2N–N$^+$/N–CH_3 imidazolium, IO_3^-	161.9	√	√	
6	H_2N–N$^+$/N–CH_3 imidazolium, IO_4^-	110.4	√	√	
7	H_2N–N$^+$/N–CH_3 imidazolium, $I_3O_8^-$	126.5	√	√	
8	H_2N–N$^+$/N–NH_2 imidazolium, IO_3^-	151.1	√	√	
9	H_2N–N$^+$/N–NH_2 imidazolium, IO_4^-	141.1	√	√	
10	H_2N–N$^+$/N–NH_2 imidazolium, $I_3O_8^-$				
11	H_3C–N$^+$/N–CH_2–N/N$^+$–CH_3 bis-imidazolium, $2IO_3^-$	124.7	√	√	
12	H_3C–N$^+$/N–CH_2–N/N$^+$–CH_3 bis-imidazolium, $2IO_4^-$				

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13	H3C–N(+)...N–CH2–N...N(+)–CH3, 4I, 2I3O8(−)	133.8	√	√	
14	H3C–N(+)...N–CH2CH2–N...N(+)–CH3, 4I, 2IO3(−)	164.0	√	√	
15	H3C–N(+)...N–CH2CH2–N...N(+)–CH3, 4I, 2IO4(−)				
16	H3C–N(+)...N–CH2CH2–N...N(+)–CH3, 4I, 2I3O8(−)	153.8	√	√	

[1]   He, C.; Zhang, J.; Shreeve, J. M. *Chem. Eur. J.* **2013**, *19*, 7503-7509.
[2]   Wu, L. P.; Yamagiwa, Y.; Kuroda-Sowa, T.; Kamikawa, T.; Munakata, M.
       Inorg. Chim. Acta **1997**, *256*, 155-159.
[3]   Xu, X.; Hu, C.-L.; Li, B.-X.; Yang, B.-P.; Mao, J.-G. *Chem. Mater.* **2014**, *26*,
       3219-3230.

iv) Opportunities for training and professional development

Research is a marvelous teaching tool for chemists at all levels. Graduate students are stimulated, guided and encouraged by postdoctoral members of the group as well as by the PI. Everyone learns more and more chemistry while concomitantly becoming familiar with modern day laboratory techniques and modern equipment, use of various softwares, and perhaps most importantly they expand their scientific communication and networking skills through everyday interactions and weekly formal research presentations. This is accomplished through using ACS-type power point presentations at weekly research group seminars that are built on the current literature and on individual monthly research progress. This practice prepares the young chemist to be at ease on his/her feet talking about chemistry in one on one or group discussions or at regional and national ACS meetings.

CONCLUSION

The goal was to produce materials that would generate low pressure and prolonged high temperature detonations destroying storage facilities and the bio-agents therein, and, secondarily, utilizing the products obtained from the blast to eradicate any harmful airborne agents which might result. Molecular or ionic solids based primarily on derivatives of polyhalides, oxohalogens, perfluorosulfanyl (SF_5) compounds, and energetic halonitroazoles were carefully prepared and characterized. By taking advantage of a list of criteria that have impact on such characteristics as density, enthalpy of formation, detonation pressure and velocity, energetic compounds were down selected.

Calculations were used to predict density and heat of formation (allowing prediction of detonation properties, specific impulse, etc.) prior to carrying out the laboratory work. The materials were thoroughly characterized in our well-equipped laboratories. Collaboration with Dr. Suhithi Peiris, GOR, and Dr. James M. Lightstone at Indian Head Division – NSWC allowed us to down select appropriate compounds to be tested on bioaeorsols and/or contained spores and thus provided Go/No Go points.

i) **Pentafluorosulfanyl derivatives**

Three pentafluorosulfanyl 1,2,3-triazoles were prepared from azides in reaction with pentafluorsulfanyl acetylene, viz.,
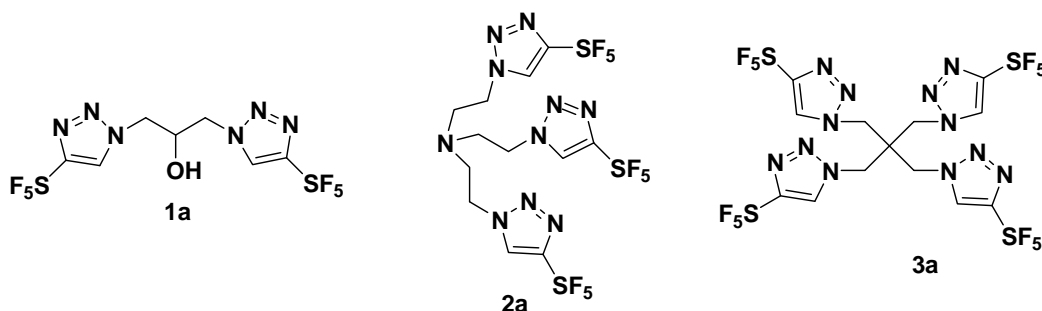
Each of these materials has a thermal stability equivalent to or exceeding TNT and is considerably denser. Their calculated detonation properties approach those of TNT while they are more than 2.5 times less sensitive to impact than is TNT. 2-(Pentafluorosulfanyl-1,2,3-triazol-1-yl)-bis-(N,N-tris(pentafluorosulfanyl-1,2,3-triazol-1-ylethyl)-ethanamine) (**2a**) was sent to Indian Head for testing. During the second year, preliminary tests were carried out; however, based on these results and the availability of other more promising materials for testing (vide infra), further work on pentafluorosulfanyl-containing compounds was terminated.

ii) **Polyiodoxyazoles**
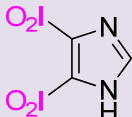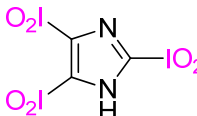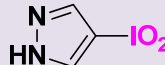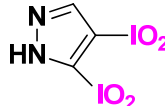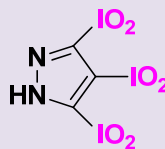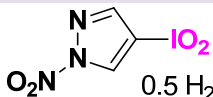
Imidazole or pyrazole-based iodoxy compounds appeared to be of interest for their high densities and thermal stabilities. Therefore, six different iodoxy compounds were synthesized and characterized. Additionally their detonation properties were calculated.

For pyrazole iodoxy derivatives, the greater the number of the iodoxy substituents, the less impact sensitive the compound. All iodoxy compounds decompose between 159 – 227 °C. The 3,4,5-tri-iodoxypyrazole (Table, entry 5) is the least thermally stable while 4,5-di-iodoxyimidazole hemihydrate (Table, entry 1) decomposed at 227 °C. As one of the most important physical properties of energetic compounds, the densities range between 2.54 – 3.68 $g \cdot cm^{-3}$. 4-Iodoxypyrazole (Table, entry 3) has a higher density then diiodoxypyrazole (Table, entry 4) which may arise from the existence of the intramolecular hydrogen bond between O10 and H5.

The heats of formation for iodoxy compounds were calculated by using the Gaussian 03 suite of programs by constructing isodesmic reactions and are summarized in the Table. The iodine atoms were optimized via mp2(full)/6-31g(d) at the ECP level,

and the heat of formation of CH_3IO_2 was calculated using G2ECP (ZPE=MP2) methodology and for other small molecules were obtained by employing the G2 method. All the compounds exhibit negative heats of formation except N-nitro-4-iodoxypyrazole which has a positive value of 54.7 kJ/mol. By using the calculated values of the heats of formation and the experimental values for the densities, the detonation velocities (D) and

Table. Physical properties of iodyl (iodoxy) compounds

Entry	Structure	m.p[a] (°C)	d[b] (g/cm^3)	ΔH_f° [c] (kJ/mol)	D[d] (m/s)	P[d] (Gpa)	IS[e] (J)
16		227	2.85	-431	4461	11.86	>40
17		183	3.68	-712	4891	16.98	5
18		201	2.99	-64.8	-	-	2
19		188	2.87	-379	4181	10.24	4
20		159	3.54	-690	4690	15.21	7
21		179	2.54	54.7	6897	28.33	12

[a] Thermal decomposition temperature under nitrogen gas (DSC, 5 °C/min^{-1}); [b] Density, measured by gas pycnometer (25 °C); [c] Heat of formation calculated with Gaussian 03; [d] Calculated detonation velocities and detonation pressures with Cheetah 6.0; [e] Impact sensitivities measured with a BAM drophammer.

detonation pressures (P) were calculated using the Cheetah 6.0 program. All the compounds have low detonation pressures that range between 10.24 to 28.33 GPa and velocities lie between 4181 to 6897 m/s comparable to the traditional energetic compounds but higher than iodo compounds. The detonation properties improve as the number of iodoxy group increases. The N-nitro group enhances the detonation properties markedly but also decreases the density.

The detonation products formed were predicted using Cheetah 6.0 under Chapman-Jouguet conditions and are shown below in weight-%. [This bar graph includes iodo compounds (1-15; pp 7-9 vide supra) and iodyl compounds (16-21)]. After detonation, most iodine atoms in these molecules are found as I_2, HI and I which are strong biocides. The molecule with more hydrogen atoms forms a high weight

percentage of HI. The sum of iodine-containing species in weight-% (I_2, HI and I, in gas phase) ranges between 46.7% (**21**) to 88.94% (**11**) as shown in the Figure below. The high percentage of these strong biocides in the detonation products makes them promising as potential bio-agent defeat
materials.

In summary, six iodoxy compounds were synthesized in moderate yields by using straightforward methods. All the compounds were confirmed by elemental analysis and characterized by IR, ^{1}H and ^{13}C NMR, elemental analysis, and differential scanning calorimetry (DSC). Detonation properties were calculated. The unique high density, high iodine content, and low detonation properties of iodoxy compounds make them interesting. The good thermal stability, moderate detonation properties and impact insensitiveness of 4, 5-diiodoxyimidazole hemihydrate makes it a candidate for a low pressure bio-agent additive. This work was terminated during year two.

iii) Polyiodides

Polyiodides have been shown to be very effective against pathogenic organisms in real life situations particularly as chemical agents that are effective in killing, for example, viruses, bacteria and eukaryotic parasites. The N-containing alkyl cations may help to increase the energy and also result in low pressure when cooperating with polyiodide anions. In our continuing interest towards seeking effective materials for bio-agent destruction, polyiodides with various symmetrical alkyl ammonium cations appeared to be good candidates.

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The iodide salts **1a - 11a** were prepared from the corresponding amine with HI or iodomethane in alcohol or acetonitrile solvent by controlling the stoichiometry of the reaction. Compounds **2b-5b**, **7b-11b**, and **9c-11c** can be prepared using a straightforward method by heating the iodide salts in appropriate amounts of elemental iodine in ethanolic solution at 50 – 60 °C. After the solvent was evaporated the residue was dried under vacuum at 50 °C overnight to obtain the corresponding polyiodide.

Most of iodide compounds have very good thermal stabilities (> 250 °C and the majority >300 °C). The iodide salts of **1a** – **11a** have an iodine content ranging from 61.29% (**11a**) to 80.34% (**1a**), and the iodine content of the polyiodide salts falls between 82.61% (**11b**) to 90.91% (**2b**). An increase in iodine content destabilizes the corresponding polyiodides (**11a** > **11b** > **11c**).

Preparation of alkyl ammonium iodide and triiodide salts

Synthesis of quaternary ammonium iodide, triiodide and pentaiodide salts
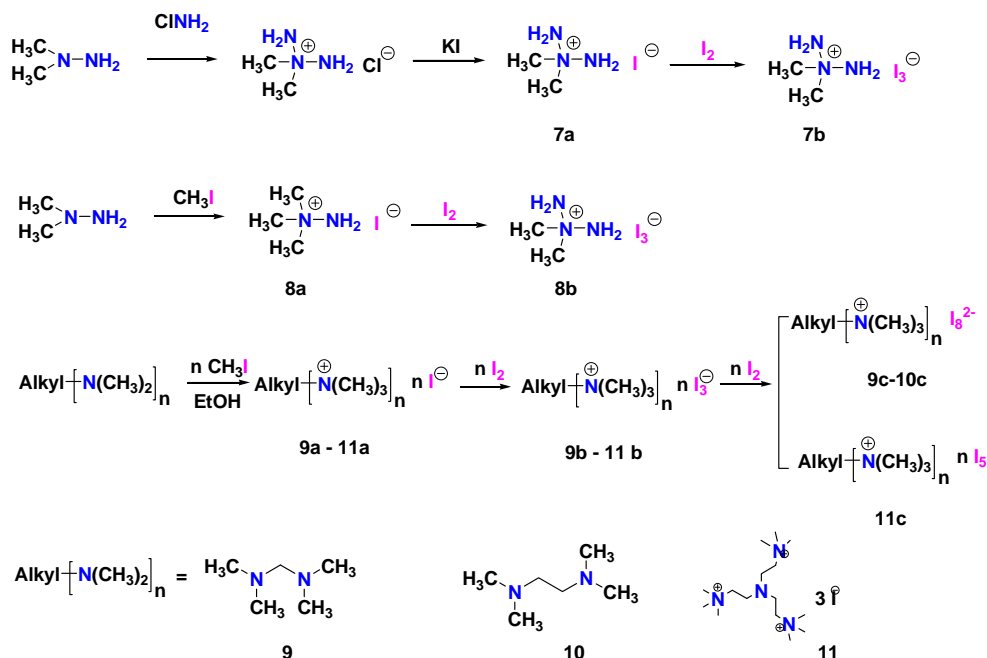
As part of the subcontract agreement with Indian Head, 20 grams of compound **11c** were submitted for preliminary testing. After shipping, it was apparently found not to be of interest.
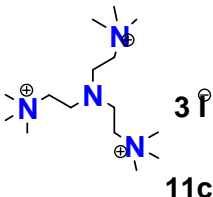
11c

In summary, during this preliminary work, 11 iodide salts and 11 polyiodide salts were synthesized. Based on measured densities and decomposition temperatures and high iodine content, the polyiodide salts appear to hold major promise as biocidal reagents. These salts appear to be attractive candidates but were never tested.

iv) Polyiodoheterocycles

a) Tetraiodofuran (TIF)

In order to achieve low pressure and prolonged high temperature detonations necessary to destroy storage facilities and bio-agents, 15 iodo compounds were prepared and characterized. All the compounds possess a high content of iodine ranging between 65.4% and 89.0% as well as good densities falling in the 2.39 g/cm^3 to 3.90 g/cm^3 range. With the increase of iodine atom numbers in a single heterocyclic ring, the density increases; iodopyrazoles are more dense than their imidazole analogues. Most of the compounds exhibit good thermal stabilities ($\geq$ 168 °C.) All of the compounds are impact insensitive (IS $\geq$28 J).

There was no information about the detonation properties of iodo compounds. Therefore, two compounds, tetraiodofuran and tetraiodopyrole, with the highest iodine content were selected to evaluate energetic properties. To obtain their heats of formation, the Gaussian 03 (D.01) program suite was employed, and isodesmic reactions were constructed. The C, H, N, O atoms were optimized at b3lyp/6-31g+ (d,p) level and iodine atoms at the Lanl2dz level. The heats of formation are summarized in the Table. By using the experimental value of the densities, the detonation properties were calculated by Cheetah 6.0. Both compounds have low detonation velocity and pressure compared to traditional explosives. The high iodine content should form various iodine-containing species after decomposition which will be biocidal.

Tetraiodofuran was selected for testing (AD mix on the outside); 2.65 grams of tetraiodofuran were submitted to Dr. Jillian Horn at Indian Head for testing which include.

- Perform small scale safety testing.
- Run 'open' air blast test to measure pressure and temperature and reaction/burn time generated.
- Based on results of air blast, decide appropriateness of bug-kill test, and if so, which one.

Preliminarily the following information was provided by Indian Head.

- Greater than 320 cm impact (low sensitivity)
- 235 psig friction (low sensitivity)
- 0.165 Joules ESD (medium sensitivity)

Table. Detonation properties of iodo compounds

Compd	HoF [a] (kJ/mol)	Density[b] (g/cm^3)	D^c (m/s)	P^c (Gpa)
Tetraiodofuran	264.3	3.83	2248	3.55
Tetraiodopyrrole	326.4	3.62	2009	2.42

[a] Heat of formation calculated with Gaussian 03; [b] Density, measured by gas pycnometer (25 °C); [c] Calculated detonation velocities and detonation pressures - Cheetah 6.0.

The major high point of our work was the further study of tetraiodofuran (TIF) which resulted in this promising material being transitioned to 6.2 for further study at China Lake, Indian Head and Elgin.

Dr. Su Peiris, GOR, in discussion with others, determined that TIF was suitable for further biocidal testing. Therefore, additional amounts of TIF were synthesized and submitted as detailed below:

Dr. Jillian Horn, Indian Head, MD   68 g
Dr. Curt Johnson, China Lake, CA   104 g   (90 g returned to UI)
Dr. Jim Lightstone, Indian Head, MD 66g

Formulation tests were undertaken at China Lake using a purified sample of TIF (vide infra). The remainder of TIF was returned to UI for further purification. The purified sample was then forwarded to Dr. Jim Lightstone at Indian Head for biocidal testing.

The results at China Lake on TIF as reported to us are reproduced exactly in the following. For further details, the report by Dr. Curtis Johnson, NAWCWD should be consulted.

"Tetraiodofuran Characterization"
Kelvin Higa and Curtis Johnson, NAWCWD, 19 April 2013

This brief report describes tests of the 104 g TIF sample received from U. Idaho 15 April 2013.

2. Boostcer Test of Al(H2*)/Bi(IO$_3$)$_3$/TIF. The Booster Test is a NAWCWD method to interrogate sample composite reactivity. A 50:50 mixture composed of a "test sample" and Al(80nm)/MoO$_3$(45nm) nanothermite is prepared, ~15 mg of the mixture is placed on an inverted Al weighing pan, and the mixture ignited with a spark. The dent in the pan (that forms in ~200 μs) is measured, and the dent attributed to the Al/MoO$_3$ is subtracted out to determine the deflection attributed to the test sample (in mm/g). Loading levels between 0 and 50% of TIF and C$_2$I$_4$ in the test sample were evaluated (see Figure below). Al(H2*), activated aluminum, is Valimet H-2 Al powder coated with 5% K$_2$AlF$_5$·H$_2$O.

Both TIF and C$_2$I$_4$ permitted high loading levels with very little change in the deflection value for the Al(H2*)/Bi(IO$_3$)$_3$/I$_2$ Source composites. These results suggest that the amount of TIF or C$_2$I$_4$ could be varied over a wide range without imposing a large effect on the reactivity of the Al(H2*)/Bi(IO$_3$)$_3$ thermite (i.e., in tests at NSWC-IHD).

Based on the earlier work carried out at Indian Head involving a non idealized formulation, a briefing presented by the Assistant Secretary of Defense for Research and Engineering to the House Armed Services Committee contained the following:

"Defense Threat Reduction Agency funded basic research at University of Idaho and two Navy Warfare Center Labs have resulted in the development of new materials for defeating targets that contain biological agents. Weapon payloads using these materials employ the dual kill mechanisms of heat and chemistry. The addition of long-burning metals, e.g., Al, and iodine-forming chemicals to the payload increases the temperature during the blast and produces iodine gas to prolong the kill of biological agents in the post-blast plume."

TIF and its properties.
Synthetic procedure

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Tetraiodofuran: Yield: 52%. M.p. 163 °C, ^{13}C NMR (DMSO-d_6): 106.2; 94.1; IR (KBr): 1700, 1497, 1444, 1242, 1084, 962 cm^{-1}. Elemental analysis: calcd for C_4HI_4N: C, 8.40; H, 0; N, 0, found: C, 8.38; H, 0.03; N, 0.10.

Crude TIF was decolorized using activated charcoal in hexane and ethyl acetate as follows: crude TIF (30.0 g) and activated charcoal (4.5 g) were added to a mixture of hexane (500 mL) and ethyl acetate (300 mL) and the final mixture was refluxed overnight. The hot solution was filtered quickly, washed with hot hexane/ethyl acetate (1:1, 100 mL), and then the filtrate was concentrated under reduced pressure recovering the organic solvent which was recycled. The pure TIF was obtained as cream needle crystals (27.2 g, 90.7 % yield).

Tips:

1. If amount of activated charcoal utilized is less than 1.5 g, TIF wasn't decolorized very well and light brown needle crystals were obtained.

2. If ethyl acetate or acetone was used separately for washing the residue without hexane, some impurities may be taken into the filtrate.

Table . Properties of TIF

	Pure TIF	Impure TIF
Melting point (°C)	163.19	162.74
Decomposition Point(°C)	289.40	271.63
EA results (Calcd: C 8. 40)	C: 8.46, H: -0.04, N: 0.06	C: 8.63, H: 0.02, N: -0.04

Since TIF (tetraiodofuran) had performed so successfully in initial tests, considerable time and effort were devoted to developing a more suitable route to TIF and to establish a method of purification which would be straightforward and rewarding. A call for six kilos of TIF was outsourced by Dr. Suhithi Peiris. This was delivered to Indian Head and further testing was undertaken.

While many alternative routes were attempted in our search for an improved straightforward route(s) to enable the synthesis of large amounts of TIF, none was superior to the original cumbersome methodology which requires considerable difficult purification, viz.,

a)

$I_2/HIO_3/H_2SO_4$

$AcOH/H_2O/CCl_4$, reflux 4days

b)

$K_2S_2O_8, H_2SO_4$

TFA/DCE

c)

KI / NaOH aq

r.t

56

d)

e)
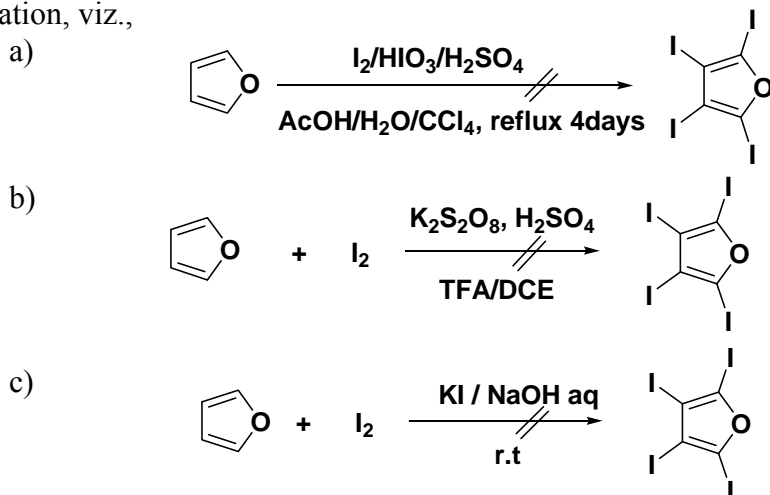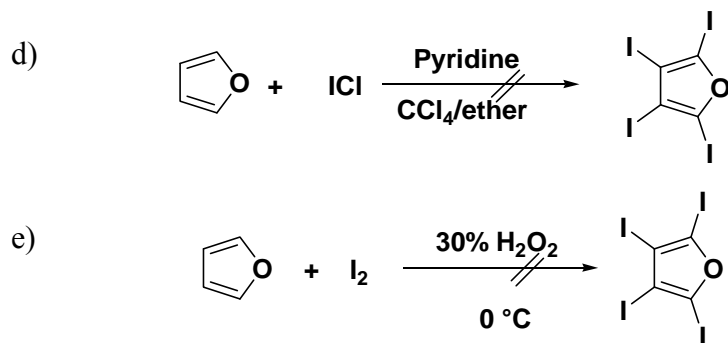
The search was continued for an environmentally friendly route.

**The TIF project is dead because the material ignited when a large batch was mixed with other ingredients. Other materials have been found in other labs subsequently for testing that are superior biocides.

b) Polyiodopyrazoles

An efficient synthesis route for polyiodopyrazoles, viz., 3, 4, 5-triiodopyrazole (**1**), 1-methyl-3, 4, 5-triiodopyrazole (**2**) and 1-diiodomethyl-3, 4, 5-triiodopyrazole (**3**) in good to excellent yields was established. The introduction of the diiodomethyl group is an effective way to increase iodine concentration. Nitration of **1** and **2** leads to the formation of the previously inaccessible 3, 4-dinitro-5-iodopyrazole (**4**) and 1-methyl-3, 4-dinitro-5-iodopyrazole (**5),** respectively, giving rise to more energetic iodopyrazoles.

Potassium persulfate was used as an oxidant using molecular iodine in the presence of trifluoroacetic and sulfuric acids to generate the electrophilic species, I^+. It is likely that only highly stable substrates could survive under these harsh conditions thus suggesting pyrazoles, known, for their stability as excellent candidates for electrophilic substitution reactions.
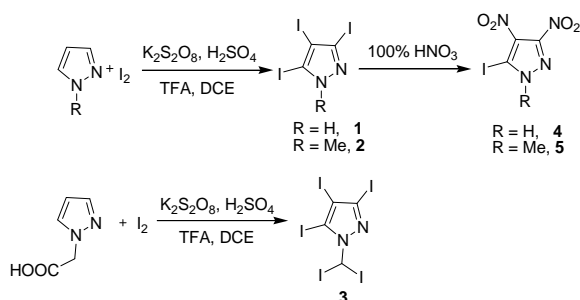
Synthesis of **1- 5**.
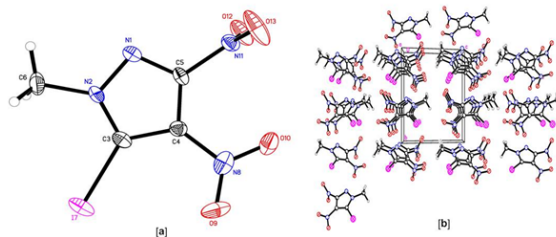
(a) Thermal ellipsoid plot (50%) of **5**. Hydrogen atoms are included but are unlabeled for clarity. (b) Ball and stack packing diagram of **5** viewed down the a-axis.

Polyiodopyrazoles, 3, 4, 5-triiodopyrazole (**1**), 1-methyl-3, 4, 5-triiodopyrazole (**2**) and N-diiodomethyl-3, 4, 5-triiodopyrazole (**3**), were synthesized in efficient electrophilic reactions; the calculated detonation properties and products suggest that the compounds may be effective bio agent defeat agents. A synthetic method was developed as an effective strategy for introducing an N-diiodomethyl group into pyrazole. Nitration of **1** and **2** with 100% HNO_3 resulted in the formation of the heretofore inaccessible iodo dinitropyrazoles, **4** and **5**. These polyiodopyrazoles may have application not only as ADWs but also in other areas such as medicinal chemistry, materials science, and synthetic organic chemistry.

v) Polyiodoheterocyclic iodides, iodates and octaoxotriiodates

The current formulations to generate the species of I, HI and /or I_2 very often contain aluminum, iodine-rich compounds (fuels) and HI_3O_8 or $Bi(I_3O_8)_3$ as an extra oxidizer. Therefore, if salts with iodine-rich cations and $I_3O_8^-$ or other oxidizing anions were obtained, they would have the advantage of reducing the amount of external oxidizer needed or without using an extra oxidizer, as well as decrease the solid residue after the decomposition.

Thirteen bromide or iodide salts with iodine-rich cations were synthesized and characterized. These were than metathesized with silver salts of oxidizing anions such as IO_3^-, IO_4^- or $I_3O_8^-$ to form 21 new high iodine-containing salts with oxidizing anions, for example,
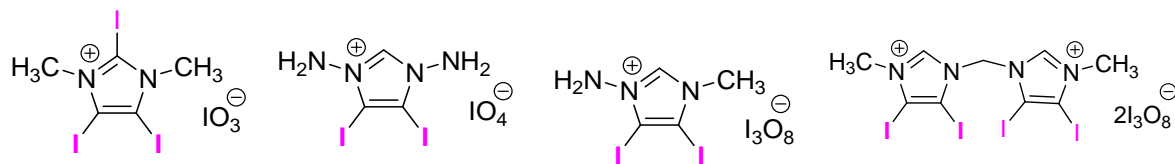
These materials are currently undergoing characterization and thermodynamic properties are being calculated. These salts hold considerable promise.

APPENDICES

1. APPENDIX A

Dense Iodine-Rich Compounds with Low Detonation Pressures as Biocidal Agents

He, C.; Zhang, J.; Shreeve, J. M. C*hemistry – a European Journal,* **2013**, *19*, 7503-7509)

Abstract: Fifteen iodo compounds and six iodyl compounds with an iodine content between 45.3% and 89.0% were prepared. The mono, di, and triiodyl compounds were obtained from the corresponding iodo compound by employing Oxone.™ All the compounds were characterized by IR, ^{1}H, and ^{13}C NMR, elemental analysis, and DSC. The impact sensitivity was measured using BAM methodology. Based on the calculated heats of formation and experimental densities, the detonation properties and detonation products were predicted by employing CHEETAH 6.0. A total percentage of iodine-containing species in weight-% (I_2, HI and I, in gas phase) ranged from 46.7% (**21**) to 88.94% (**11**) was found in the detonation products. The high concentration and easy accessibility of iodine and/or iodine-containing species is very important in developing materials suitable as Agent Defeat Weapons.

Introduction

During the last few years, interest in developing Agent Defeat Weapons (ADWs) has grown in order to enable the minimization of the collateral damage arising from chemical and biological weapons.[1] The low pressure and prolonged high temperature detonations generated by ADWs destroy storage facilities and the bio-agents therein, and, secondarily, utilize the materials arising from the blast to eradicate any harmful airborne agents which may have resulted. It has been shown that hydroiodic acid (HI) and iodine (I_2) have strong biocidal activity against biological agents.[2] Therefore, iodine-rich compounds which could generate HI or I_2 upon detonation are of interest as ingredient candidates for ADWs.

Polyiodo compounds such as triiodoimidazole,[3] tetraiodofuran,[4] tetraiodopyrrole, etc., have high iodine contents, high densities and good thermal stabilities. However, there is no information about properties such as impact sensitivity, heat of formation and detonation properties. The expected low detonation pressures and low energy of these polyiodo compounds make them worthwhile candidates for ADWs (Figure 1). The iodyl group ($-IO_2$) is an attractive functional group which possesses a structure similar to that of the nitro group and which can be produced by oxidizing the corresponding iodo compound. Iodyl compounds are likely to be more energetic than the corresponding iodo compounds. The densities of ammonium periodate[5] (density, 3.04 g/cm^3) and ammonium iodate (density, 3.30 g/cm^3) suggest that such oxohalogens may exhibit useful attributes with higher densities than the perchlorates and also with great effectiveness toward bio-agents and with less negative environmental impacts. However, most of the research concerning iodyl compounds is focused on the synthesis and applications of 2-iodylbenzoic acid (IBX) and its analogues based on the advantages provided by their selective, mild, and environmentally friendly properties as oxidizing

agents in organic synthesis.[6] Iodyl pyridines are the only N-heterocyclic iodyl compounds in the literature.[7] Iodyl-substituted imidazole or pyrazole-based compounds could be of interest because of their high densities and greater thermal stabilities. Although some explosions of iodyl compounds have been reported in the literature,[8] these materials have not been studied systematically as energetic compounds.

10   **13**   **17**
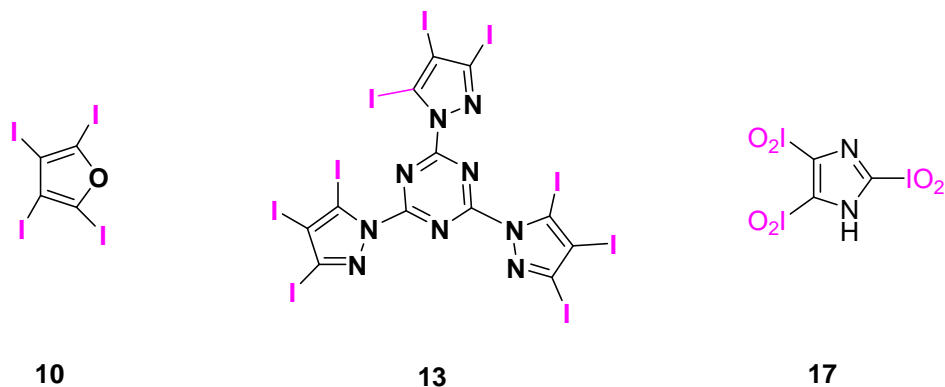
Figure 1. Iodo and iodyl compounds of interest as ADWs.

The iodine-rich iodo and iodyl compounds could be interesting ingredient candidates for ADWs (Figure 1). In our continuing search for novel energetic compounds, 15 iodo compounds and six iodyl compounds were synthesized using straightforward methods and characterized by IR, NMR, elemental analysis, and differential scanning calorimetry (DSC). Densities were measured and heats of formation were determined which made the calculation of detonation properties possible.

Results and Discussion

Mono-, di-, tri- and tetra-iodo-substituted compounds **1-11** were prepared based on the literature.[3-4, 9] For the preparation of **12-15**, the respective iodo compound (3.5 eq) was refluxed with potassium carbonate (7.7 eq) in dry CH_3CN under nitrogen for 1 h; then cyanuric chloride (1 eq) was added and the solution was refluxed for 2-8 h to complete the reaction (Scheme 1).
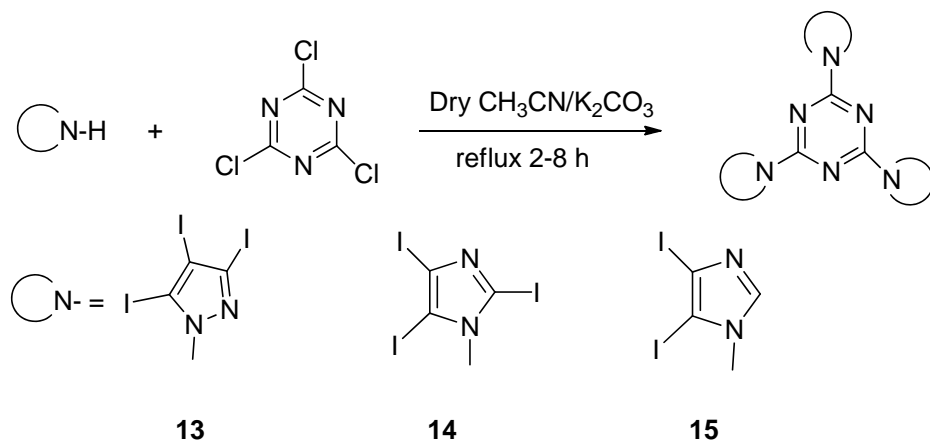
13   **14**   **15**

The common oxidants that have been used for preparing iodyl compounds include sodium hypochlorite, sodium periodate, dimethyldioxirane, and Oxone[TM] (potassium peroxomonosulfate).[10] Based on the low cost, commercial availability and its good stability, simple handling and non-toxic nature, Oxone[TM] was used in preparation of the iodyl compounds using a modified method (Scheme 2).[10b] While oxidation of mono iodo compounds can be accomplished in aqueous solution at room temperature using 1.3 eq Oxone[TM], oxidation of poly iodo compounds requires temperatures up to 70 °C and often extended reaction times to complete the reactions. All of the iodyl compounds are slightly or totally insoluble in water which allows them to be precipitated and easily purified by washing with cold water. However, after striving to oxidize all of the 15 iodo compounds, only five iodyl compounds (**16-20**) were obtained successfully. The attempted oxidization reactions of the N-acetyl compounds (**4** and **12**) as well as of compounds **13-15** failed due to steric effects with the starting material being recovered; oxidation of **5** and **8** generated products with good solubility in water which were difficult to isolate. The more energetic iodyl nitropyrazole compound **21** was synthesized by nitrating **18** using 100% HNO_3 (See Supporting Information). All of the iodo and iodyl compounds were characterized by IR, NMR, elemental analysis and differential scanning calorimetry (DSC). NMR data were not obtained for **19** and **20** due to lack of solubility in any available solvent. Single crystals for X-ray analysis were not obtained because solvents suitable for recrystallization could not be found.

16-20

16 **17** **18**

19 **20**

18 **21**
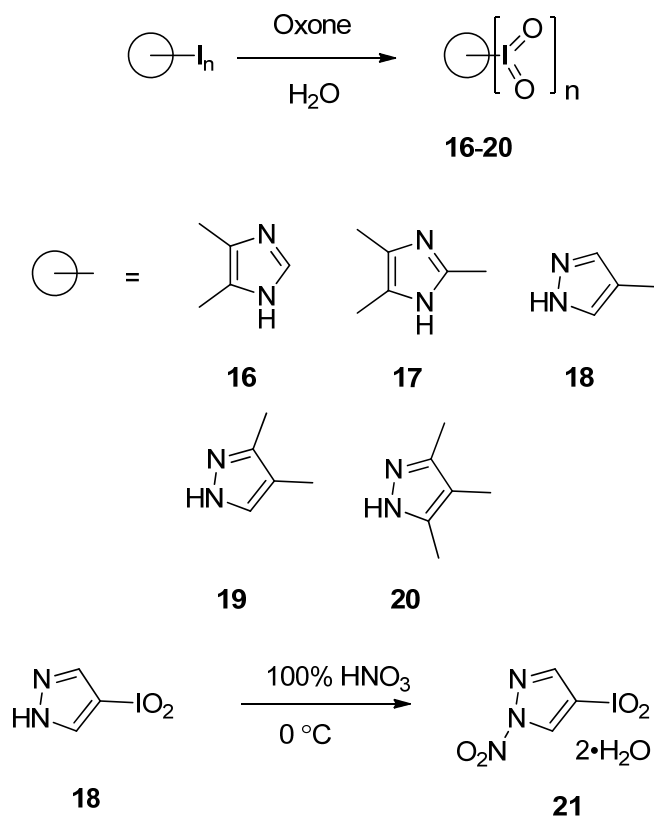
Scheme 2. Preparation of iodyl compounds.

Physical properties of the iodo and iodyl compounds are listed in Tables 1 and 2. All of the iodo compounds possess high iodine contents ranging from 65.4% to 89.0% and exhibit densities from 2.39 g/cm^3 to 3.90 g/cm^3. Increase of iodine atom numbers in single heterocyclic rings concomitantly results in increase of density. Iodopyrazoles are more dense than their imidazole analogues; all compounds exhibit good thermal stabilities (≥ 168 °C, **11**). Compounds **1-10** melt before they decompose thermally while **11-15** decompose without melting. The thermal stabilities of trisubstituted triazine compounds (**13-15**) are superior relative to their parent iodo compounds due to their symmetric structures. Methyl derivatives have lower melting points and higher decomposition temperatures while the presence of the carboxylic acid group gives rise to decreased thermal stability and density. The densities of iodyl compounds range between 2.54 – 3.68 g/cm^3. Surprisingly, 4-iodylpyrazole (**18**) has a higher density than its diiodo analogue, diiodylpyrazole (**19**), which may arise from an intramolecular hydrogen bond between O10 and H5 (2.821 Å - Figure 3, dashed line) based on the optimized structure calculated using the Gaussian 03 program. All iodyl compounds decomposed between 159 – 227 °C; triiodyl compound **20** is the least thermally stable while compound **16** decomposes at 227 °C probably arising from hydrogen bond formation as a result of the presence of water as the hemihydrate.

Impact sensitivity measurements were made using standard BAM techniques.[11] All the iodo compounds have relatively low impact insensitivities (IS ≥28 J); however, the iodyl compounds have impact sensitivities ranging between 2 to 40 J. Compound **16** shows an impact sensitivity lower than expected which arises from the presence of water which is involved in forming extensive hydrogen bonds. Water of hydration in **21** also improves the impact sensitivity to some extent. For pyrazole iodyl derivatives, the more iodyl groups in the compounds, the less impact sensitive the compound is. Based upon electrostatic potential (ESP) calculations, **18** has wider and stronger positive potentials, and **20** has the weakest positive potentials compared to **18** and **19**, which suggests that **18** should be the most sensitive and **20** the least sensitive towards impact (Figure 3). The calculated results are in agreement with the experimental results. With the exception of **10** and **11** which have impact sensitivities of 35 J and 28 J, respectively, the impact sensitivities of all of the iodo compounds exceed 40 J.
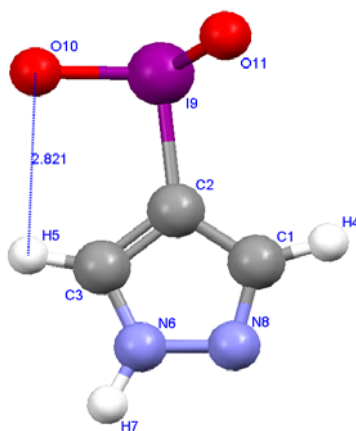
Figure 2. Intramolecular hydrogen bond in 4-iodylpyrazole (B3LYP/6-31G+**).
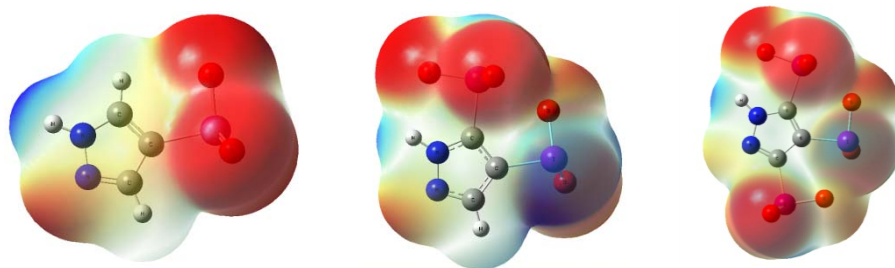
Figure 3. Electrostatic potentials (ESPs) of **18, 19, 20** for the 0.001 electron/bohr^3, ranging from -0.03 (red) to +0.05 (dark blue) hartrees.

The heats of formation for all the compounds were calculated using Gaussian 03 (Revision D.01) program suite[12] by constructing isodesmic reactions and are summarized in Tables 1 and 2. For iodine-containing species, the (15s, 11p, 6d) basis of Stromberg *et al.*[13] was augmented with another p shell and the five valence sp exponents optimized, resulting in a [5211111111,411111111,3111] contraction scheme in conjunction with 6-31+G** for first- and second-row elements. Single point energy (SPE) refinement on the optimized geometries was performed with the use of MP2/6-311++G** level. Corresponding iodine sets were constructed in MP2 method using all-electron calculations and quasi relativistic energy-adjusted spin-orbit-averaged seven-valence-electron effective core potentials (ECPs). The heats of formation of some simple aliphatic iodo compounds and iodobenzene were calculated and the results agree well with their experimental data (See Supporting Information).[14]

As shown in Table 1, all of the iodo compounds have positive heats of formation that range between 288.0 – 2019.6 kJ/mol. The heats of formation increase as the number of iodine atoms increases; each time an additional iodine atom was introduced into a pyrazole or imidazole ring the heat of formation of the molecule was increased by 62-64 kJ/mol. However, all of the iodyl compounds except **21** with a positive value of 94.9 kJ/mol exhibit negative heats of formation. The value becomes more negative with the increasing number of iodyl groups in the molecule. By using the calculated values of the heats of formation and the experimental values for the densities, the detonation velocities (*D*) and detonation pressures (*P*) were calculated using the Cheetah 6.0 program. All the compounds have low detonation pressures which range between 3.27 to 23.11 GPa and detonation velocities lie between 2253 to 6166 m/s. Except for **21** which has detonation properties comparable to TNT, the other compounds exhibit low detonation pressures and velocities which are desirable for ADWs. However, the values of the detonation properties increase as the number of iodyl groups increases; introduction of a nitro group by N-nitration enhances the magnitude of the detonation properties markedly and also decreases the density to some extent.
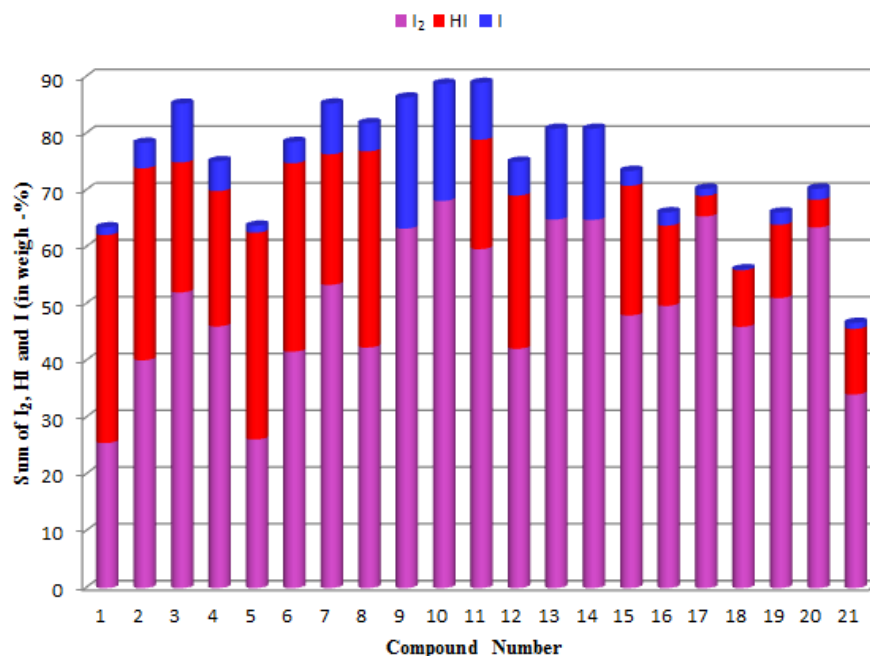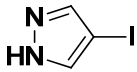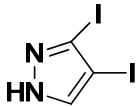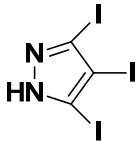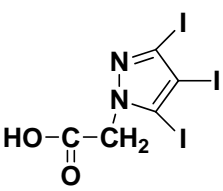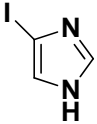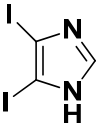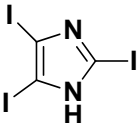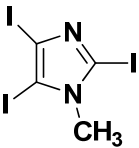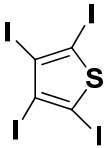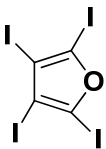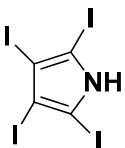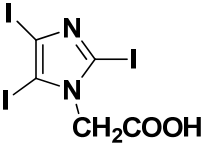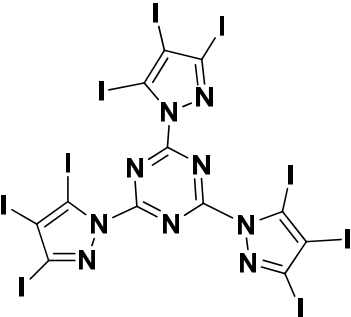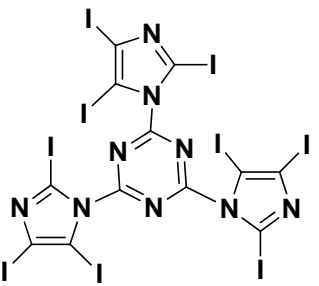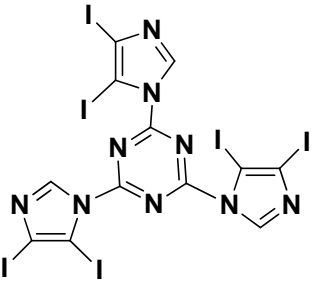
Figure 4. The sum of iodine-containing species in the detonation products (weight percent).

The detonation products formed were predicted using Cheetah 6.0 under Chapman-Jouguet condition and are listed in Table 3 in weight-%. After detonation, most iodine atoms in the molecule are found as I_2, HI and I which are strong biocides. The molecule with more hydrogen atoms forms a high weight percentage of HI. The species CO_2 and CO in weight-% increase as a function of the increase in oxygen balance. The sum of iodine containing species in weight-% (I_2, HI and I, in gas phase) ranges between 46.7% (**21**) to 88.94% (**11**) as shown in Figure 4. The high percentage of those strong biocides in the detonation products makes them promising as potential bio-agent defeat materials.

Table 1. Physical properties of iodo compounds
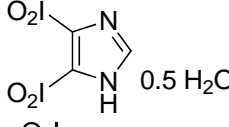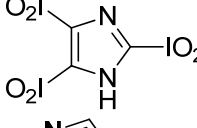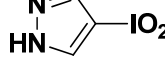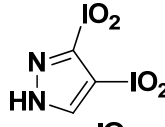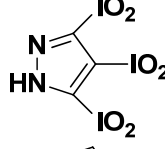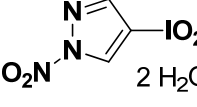
Comp	Structure	T_m [a] (°C)	T_d [b] (°C)	d [c] (g/cm³)	ΔH_f° [d] (kJ/mol)	ΔH_f° (kJ/g)	OB [e] (%)	D [f] (m/s)	P [g] (Gpa)	% Iodine
1		109	229	2.48	337.3	1.74	-61.8	4210	9.46	65.4
2		160	290	3.14	400.3	1.25	-35.0	3475	7.63	79.4
3		220	282	3.38	461.1	1.03	-23.3	2859	5.32	85.4

64

#									
4		237	247	3.27	396.4	0.79	-30.2	4049	11.41	75.6
5		137	220	2.39	288.0	1.48	-61.8	3912	7.82	65.4
6		197	233	3.09	351.9	1.10	-35.0	3298	6.68	79.4
7		191	252	3.27	416.0	0.93	-23.3	2646	4.37	85.4
8		153	318	3.26	477.0	1.04	-26.1	3137	6.35	82.8
9		204	397	3.94	547.1	0.93	-136.1	2304	4.03	86.4
10		163	261	3.83	341.0	0.60	-19.6	2417	4.29	88.8
11		[h]	168	3.62	449.9	0.79	-23.8	2253	3.27	89.0
12		[h]	180	3.00	360.6	0.72	-30.2	3658	8.74	75.6

	Structure		[a]	[b]	[c]	[d]	[e]	[f]	[g]	
13		h		355	3.30	2019.6	1.43	-27.2	3223	6.64	80.9
14		h		315	3.10	1881.3	1.33	-27.2	2894	5.07	80.8
15		h		386	3.05	1250.9	1.21	-39.4	3554	7.22	73.6
TNT	-	h		295	1.65	-67	-0.3	-31.7	6881	19.53	-

[a] Melting point; [b] Decomposition temperature; [c] Density, measured by gas pycnometer (25 °C); [d] Heat of formation calculated with Gaussian 03; [e] Oxygen Balances. [f] Calculated detonation velocities with Cheetah 6.0; [g] Calculated detonation pressures with Cheetah 6.0; [h] Decompose before melting.

Table 2. Physical properties of iodyl compounds

Compd	Structure	T_d[a] (°C)	d[b] (g/cm³)	ΔH_f°[c] (kJ/mol)	ΔH_f° (kJ/g)	OB[d] (%)	D[e] (m/s)	P[f] (Gpa)	% Iodine	IS[g] (J)
16	O2I, N, O2I, N–H · 0.5 H2O	227	2.85	-388.8	-1.01	-12.2	4129	9.89	64.6	>40
17	O2I, N, IO2, O2I, N–H	183	3.68	-669.3	-1.23	-1.5	4946	17.60	70.3	5
18	N, HN, IO2	201	2.99	-24.2	-0.11	-24.8	5505	19.09	56.2	2
19	IO2, N, IO2, HN	188	2.87	-336.9	-0.88	-12.5	4457	12.22	66.1	4
20	IO2, N, IO2, HN, IO2	159	3.54	-647.3	-1.19	-1.5	4746	15.79	70.3	7
21	N, N, IO2, O2N · 2 H2O	179	2.54	94.9	0.35	-15.6	6166	23.11	45.3	12
TNT	-	295	1.65	-67	-0.3	-31.7	6881	19.53	-	15

[a] Decomposition temperature; [b] Density, measured by gas pycnometer (25 °C); [c] Heat of formation calculated with Gaussian 03; [d] Oxygen balances; [e] Calculated detonation velocities with Cheetah 6.0; [f] Calculated detonation pressures with Cheetah 6.0; [g] Impact sensitivities measured by BAM drophammer.

Table 3. Major detonation products of iodo or iodyl compounds (in weight %, kg/kg)

compd	N_2 (g)	I_2 (g)	HI (g)	I (g)	C (s)	CO (g)	CO_2 (g)
1	11.92	25.54	36.64	1.34	16.21	-	-
2	8.07	40.11	33.83	4.45	10.60	-	-
3	6.22	52.07	22.87	10.34	8.00	-	-
4	4.88	46.08	23.83	5.24	9.73	1.33	4.07
5	12.19	26.17	36.41	1.21	16.07	-	-
6	8.08	41.62	33.19	3.74	10.58	-	-
7	6.23	53.40	22.99	8.92	8.00	-	-
8	5.48	42.37	34.53	4.96	9.67	-	-
9	-	63.30	-	23.07	7.94	-	-
10	-	68.18	-	20.62	6.99	1.70	2.52
11	2.43	59.70	19.25	9.99	8.37	-	-

12	5.07	42.13	26.99	5.96	7.62	2.24	3.92
13	8.93	64.89	-	15.98	10.21	-	-
14	8.93	64.81	-	16.06	10.21	-	-
15	11.88	48.00	22.84	2.61	13.80	-	-
16	6.94	49.69	14.13	2.33	3.93	0.72	18.03
17	4.87	65.45	3.61	1.24	0.28	0.05	22.45
18	10.40	46.00	9.96	0.17	13.05	0.04	7.23
19	6.77	51.06	12.91	2.17	3.88	0.62	17.87
20	4.89	63.48	4.89	1.94	0.23	0.14	22.49
21	12.05	34.08	11.57	1.05	-	2.57	21.18

Conclusion

In summary, 15 iodo compounds and six iodyl compounds were synthesized using straightforward methods. All the compounds were characterized by IR, ^{1}H and ^{13}C NMR, elemental analysis and differential scanning calorimetry (DSC), and the detonation products, and physical and detonation properties were obtained. The uniquely high density, the high I_2, HI and I concentrations present in the detonation products, and the low detonation pressures make these materials promising candidates as ingredients in ADWs. Compound 16 might be used as an oxidant in organic synthesis because of its insensitive properties. The iodyl compounds which have high densities, good thermal stabilities, and impact sensitive properties could be considered as primary explosives.

Experimental Section

Caution: Although no problems have been encountered during these syntheses, all the iodyl compounds described in this paper are potential energetic compounds and tend to explode under certain conditions. Appropriate safety precautions should be taken when preparing.

General Methods: Reagents are commercially available from Aldrich and Acros Organics and were used as received. ^{1}H and ^{13}C NMR spectra were recorded on a 300 MHz (Bruker AVANCE 300) nuclear magnetic resonance spectrometer operating at 300 and 75.48 MHz, respectively, by using DMSO-d_6 and D_2O as solvents and locking solvent unless otherwise stated. The melting and decomposition points were obtained on a differential scanning calorimeter (TA Instruments Co., model Q10) at a scan rate of 5 °C min^{-1}. TGA (TA Instruments Co., model 50) measurements were carried out by heating samples at 10 °C/min from 25 to 600 °C. IR spectra were recorded using KBr pellets for solids on a BIORAD model 3000 FTS spectrometer. Densities of the iodyl compounds

were measured at 25 °C by employing a Micromeritics AccuPyc 1330 gas pycnometer. Elemental analyses were obtained by using an Exeter CE-440 elemental analyzer. 4,5-Diiodoimidazole,[3] 2,4,5-triiodoimidazole,[3] 4-iodopyrazole,[9a] 3,4-diiodopyrazole,[9b] and 3,4,5-triiodopyrazole[9b] were prepared according to literature procedures.

4-Iodopyrazole (1):[9a] Prepared according to the literature method, yield 65%. M.p.: 109 °C, T_{dec}: 229 °C, ^{1}H NMR: 13.13, 7.77 ppm; IR (KBr): 3115, 3040, 2954, 2911, 2846, 1533, 1364, 1321, 1261, 1175, 1142,1032, 935, 872, 811, 649, 608 cm^{-1}.

4, 5-Diiodopyrazole (2):[9b] Prepared according to the literature method; product was washed with aqueous ammonia and air dried, yield 40%. M.p.: 160 °C, T_{dec}: 290°C., ^{1}H NMR: 13.49, 7.83 ppm; IR (KBr): 3126, 3022, 2926, 2850, 2781, 2709, 1323, 1254, 1175, 1059, 968, 942, 854, 806, 604 cm^{-1}.

3,4,5-Triiodopyrazole (3):[9b] Yield 10%. M.p.: 220 °C, T_{dec}: 282 °C, ^{1}H NMR: 13.94; IR (KBr): 3073, 2949, 2872, 2816, 27311512, 1315, 1242, 1131, 961, 854, 807, 604, 447 cm^{-1}.

3, 4, 5-Triiodopyrazolyl-1-acetic acid (4):[9b] Yield, 72%. M.p.: 237 °C, T_{dec}: 247 °C, ^{1}H NMR: 13.48, 5.09 ppm.

4(5)-Iodoimidazole (5):[15] Yield 93%. M.p.: 137 °C, T_{dec}: 220 °C. ^{1}H NMR: 7.31, 7.62 ppm; IR (KBr): 3442, 3105, 2997, 2875, 2805, 2683, 2641, 2600, 1795, 1435, 1291, 1166, 1128, 1070, 955, 820, 620, 495 cm^{-1}.

4, 5-Diiodoimidazole (6):[3] Prepared according to the literature method, recrystallized from EtOH and water, yield 42%. M.p.: 197 °C, T_{dec}: 233 °C, ^{1}H NMR: 12.90, 7.77 ppm; IR (KBr): 3078, 2960, 2776, 2648, 2584, 2480, 1812, 1639, 1542, 1454, 1285, 1271, 1179, 1152, 955, 918, 818, 654, 620 cm^{-1}.

2,4,5-Triiodoimidazole (7):[3] Prepared according to the literature method using four equivalents I$_2$, recrystallized from 95% EtOH, yield 90%. M.p.: 191°C, T_{dec}: 252 °C, ^{1}H NMR: 13.34; IR (KBr): 3421, 3026, 2930, 2831, 2741, 2644, 2583, 1503, 1374, 1269, 1161, 971, 656, 436 cm^{-1}.

1-Methyl-2,4,5-triiodoimidazole (8): Modification of a literature procedure;[16] potassium carbonate (0.61 g, 4.4 mmol) and 2,4,5-triiodoimidazole (0.90 g, 2 mmol) were added to 10 mL CH$_3$CN; 0.14 mL (2.2 mmol) CH$_3$I was then added slowly to the above mixture. The reaction mixture was stirred overnight, then poured into 30 g ice water, filtered and dried to give 0.88 g white solid, yield 95%. M.p.: 153 °C, T_{dec}: 318 °C. ^{1}H NMR: 3.65 ppm; ^{13}C NMR: 39.33, 88.49, 94.74, 97.50 ppm; IR (KBr): 2932, 1431, 1373, 1343, 1190, 1099, 1067, 947, 706, 422 cm^{-1}. Anal. calcd for C$_3$H$_3$I$_3$N$_2$: C 10.45, H 0.66, N 6.09; found: C 10.47, H 0.60, N 5.80.

Tetraiodothiophene (9):[17] Starting from 2-iodothiophene using a modified method, yield: 85%. M.p.: 203 °C, T_{dec}: 397 °C, IR (KBr): 1648, 1433, 1362, 1219, 1169, 1027, 954, 696 cm^{-1}. Anal. calcd for C$_4$I$_4$S: , C, 8.17; H, 0; N, 0; found: C, 8.14; H, 0; N, 0.78.

Tetraiodofuran (10): [4] Prepared according to the literature, yield: 52%. M.p.: 163 °C, T_{dec}: 261 °C, ^{13}C NMR: 106.2; 94.1 ppm; IR (KBr): 1700, 1497, 1444, 1242, 1084, 962, cm^{-1}. Anal. calcd for C_4HI_4N: C, 8.40; H, 0; N, 0, found: C, 8.38; H, 0.03; N, 0.10.

Tetraiodopyrrole (11): The same method as used for **10**, yield: 47%. T_{dec}: 168 °C, ^{1}H NMR: 12.3; ^{13}C NMR: 86.7; 79.7. IR (KBr): 3431, 1530, 1375, 1292, 1170, 1027, 963, 897, 865, 772, 667 cm^{-1}. Anal. calcd for C_4HI_4N: C, 8.42; H, 0.18; N, 2.45; found: C, 8.68; H, 0.17; N, 2.46.

2,4,5-Triiodoimidazolyl-1-acetic acid (12): The mixture of potassium carbonate (0.61 g, 4.4 mmol), 2,4,5-triiodoimidazole (0.90 g, 2 mmol) and bromoacetate (2.2 mmol) in 25 mL 2-ethoxyethanol was heated at 100 °C for 16h; the suspension was filtered and the filtrate was evaporated under reduced pressure. The residue was dissolved in water, the solution was filtered, and the filtrate acidified to pH 1 to give 2,4,5-triiodoimidazolyl-1-acetic acid, 0.75 g, yield 69%. T_{dec}: 179 °C, ^{1}H NMR: 4.79, 13.53 ppm; IR (KBr): 3427, 1717, 1458, 1418, 1356, 1328, 1238, 1173, 982, 889, 803, 669, 446 cm^{-1}. Anal. calcd for $C_5H_3I_3N_2O_2$: C 11.92, H 0.60, N 5.56; found: C 11.95, H 0.60, N 5.48.

General procedure for preparing tris(3, 4, 5-triiodopyraolyl) -2, 4, 6-triazine (13), tris(2, 4, 5-triiodoimidazolyl) - 2, 4, 6-triazine (14) and tris(4, 5-diiodoimidazolyl)-2, 4, 6-triazine (15): the respective iodo compound (3.5 eq) and potassium carbonate (7.7 eq) were refluxed in CH_3CN for 1 h; then cyanuric chloride (1 eq) was added in portions, and heating continued for 2-8 h to complete the reaction. The reaction mixture was cooled to room temperature, filtered and the filter cake was washed with CH_3CN, followed by water. Then it was air dried to give the expected product.

Tris(3, 4, 5-triiodopyraolyl) -2, 4, 6-triazine (13): yield 80%. M.p.: T_{dec}: 355 °C, ^{13}C NMR: 162.9; 118.0; 98.56; 98.50 ppm; Anal. calcd for $C_{12}I_9N_9$: C 10.21, H 0, N 8.93; found: C 10.49, H 0.11, N 8.08.

Tris(2, 4, 5-triiodoimidazolyl) - 2, 4, 6-triazine (14): yield 85%. T_{dec}: 386 °C, ^{13}C NMR: 162.4; 106.1; 95.2; 86.6; IR (KBr): 1547, 1456, 1382, 1274, 1163, 1065, 945, 808, 688, 648 cm^{-1}. Anal. calcd for $C_{12}I_9N_9$: C 10.21, H 0, N 8.93; found: C 10.23, H 0.02, N 8.57.

Tris(4, 5-diiodoimidazolyl)-2, 4, 6-triazine (15): yield 73%. M.p.: 386 °C (dec), ^{1}H NMR: 9.00 ppm; ^{13}C NMR: 39.33, 88. 49, 94.74, 97.50 ppm; Anal. calcd for $C_{12}H_3I_6N_9$: C 13.93, H 0.29, N 12.18; found: C 14.24, H 0.31, N 11.89.

General procedure for preparing iodyl compounds: 0.8 g (1.3 mmol) of Oxone^{TM} was dissolved in 5 mL H_2O at room temperature, then 1 mmol of mono iodo compound was added in portions. The reaction mixture was stirred for 3 h, the precipitate formed was collected by filtration, washed by 2 mL cold water then 1 mL acetone, and air dried. Double or triple quilities of Oxone^{TM} and water were needed to prepare di or tri-iodyl compounds, heating at 70 °C and stirring overnight were required to complete the reaction.

4, 5-Di-iodylimidazole hemidyrate (16): yield: 64.3%, 124 °C (-H_2O), T_{dec}: 228 °C. ^{1}H NMR: 8.38 (d, CH) ppm; ^{13}C NMR: 141.3 (C-IO_2), 85.9 (C=N) ppm; IR (KBr) 3462 (-OH), 3148 (-NH), 3050, 2914, 2820, 2747, 2577, 1871, 1643, 1566, 1148, 1101, 1065, 887, 822 (I=O), 617, 513 cm^{-1}. Anal. calcd for $C_3H_2N_2I_2O_4 \cdot 0.5H_2O$: C 9.17, H 0.77, N 7.13; found: C 9.53, H 0.86, N 7.21.

2, 4, 5-Tri-iodylimidazole (17): yield: 55.6%, T_{dec}: 183 °C. IR (KBr): 3447 (NH), 1655, 1439, 1324, 1277, 1215, 1175, 982, 473 cm^{-1}. Anal. calcd for $C_3H_1N_2I_3O_6$: C 6.65, H 0.19, N 5.17; found: C 7.06, H 0.13, N 5.27.

4-Iodylpyrazole (18): yield: 72.6%, T_{dec}: 201 °C. ^{1}H NMR (D_2O) 8.25 (s, CH) ppm; ^{13}C NMR (D_2O) 136.0 (C-IO_2) ppm, 124.9 (C=N); IR (KBr) 3160 (-NH), 3096, 3055, 2963, 2872, 2829, 1558, 1482, 1380, 1329, 1171, 1153, 1031, 957, 838, 802, 773(I=O), 725, 615 cm^{-1}. Anal. calcd for $C_3H_3N_2IO_2$: C 15.95, H 1.34, N 12.40; found: C 16.08, H 1.22, N 11.86.

3,4-Di-iodylpyrazole(19): yield:73.4%, T_{dec}: 188 °C. IR (KBr) 3229 (-NH), 3142, 2975, 2911, 1630, 1501, 1443, 1351, 1247, 1154, 1097, 1061, 970, 931, 727 (I=O), 687, 613 cm^{-1}. Anal. calcd for $C_3H_3N_2I_2O_4$: C 9.39, H 0.53, N 7.30; found: C 9.13, H 0.78, N 6.86.

3, 4, 5-Tri-iodylpyrazole (20): yield: 73.4%, T_{dec}: 159 °C. IR (KBr) 3162, 3140 (-NH), 2923, 1568, 1522, 1451, 1395, 1349, 1327, 1209, 1161, 1049, 972, 931, 854, 822, 787 (I=O), 604 cm^{-1}. Anal. calcd for $C_3H_3N_2I_2O_4 \cdot 2.5H_2O$: C 6.14, H 1.03, N 4.77; found: C 6.23, H 0.91, N 4.40.

Procedure for preparing N-nitro-4-iodylpyrazole (21): 0.1 g 4-iodopyrazole was added in portions to 2 mL 100% HNO_3 with cooling. The reaction mixture was stirred at 0 °C for 1.5 h, and then poured into 5 g ice water. The solid which formed was collected by filtration and dried under vacuum to give 0.108 g white solid, yield 92%.

N-nitro-4-iodylpyrazole dihydrate (21): T_{dec}: 132(-H_2O) 179 °C, ^{1}H NMR: 8.05, 8.10 ppm. IR (KBr) 3392 (-OH), 1630, 1381, 1184, 1128, 1042, 947, 854, 741 (I=O), 602 cm^{-1}. Anal. calcd for $C_3H_2N_3I_1O_4 \cdot 2H_2O$: C 11.74, H 1.97, N, 13.69; found: C 11.73, H, 1.81, N 13.03.

Acknowledgements

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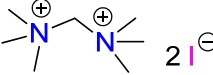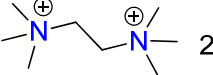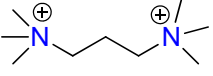
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[11]   a) www.bam.de. b) The sample is placed between two steel cylinders that are fixed by a steel ring, a 10 kg weight BAM hammer is falling from a height at which the samples decompose or explode, the reported impact sensitivity value is the fall energy, given in J. The range in impact sensitivities according to the UN Recommendations is: insensitive >40 J; less sensitive ≥35 J; sensitive ≥4 J; very sensitive ≤3 J.

[12]   Gaussian 03 (Revision D.01): M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E.Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin,J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi,G. Scalmani, N. Rega, G. A. etersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R.Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene,X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R.Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W.Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G.Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D.Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L.Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M.Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A.Pople, Gaussian, Inc., Wallingford CT, 2004.

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APPENDIX B   Synthesis and characterization of polyiodide compounds
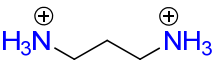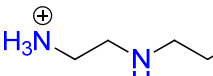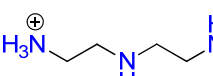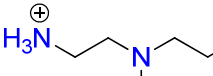
Table 1. Physical properties of iodide compounds (thermodynamic properties to be determined).
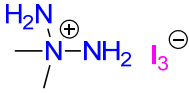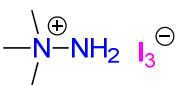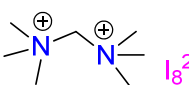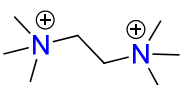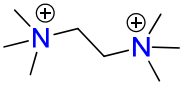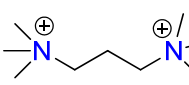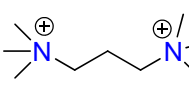
Compd	Structure	T_m [a] (°C)	T_d [b] (°C)	d [c] (g/cm³)	ΔH_f° [d] (kJ/mol)	ΔH_f° (kJ/g)	OB [e] (%)	D [f] (m/s)	P [g] (Gpa)	% Iodine
1a		332.8	336.6	2.75			-40.5			80.34
2a		257.1	307.2	2.52			-53.3			76.92
3a		240.5	295.2	2.34			-64.6			70.70
4a		192.3	318.2	2.07			-63.6			63.13
5a		318.1	322.8	2.44			-63.4			71.84
6a		303.2.0	342.0	2.46			-44.7			78.84
7a		133.0	176.0	2.05			-67.0			62.51
8a		316.0	-	1.87			-95.3			65.74

Compd	Structure	T_m [a] (°C)	T_d [b] (°C)	d [c] (g/cm³)	ΔH_f° [d] (kJ/mol)	ΔH_f° (kJ/g)	OB [e] (%)	D [f] (m/s)	P [g] (Gpa)	% Iodine
9a		-	239.5	1.84			-87.1			62.81
10a		274.5	278.7	1.83			-104.0			63.44
11a		304.8	-	1.73			-112.1			61.29
										-
TNT	-	h	295	1.65	-67	-0.3	-31.7	6881		19.53

[a] Melting point; [b] Decomposition temperature; [c] Density, measured by gas pycnometer (25 °C); [d] Heat of formation calculated with Gaussian 03; [e] Oxygen Balances. [f] Calculated detonation velocities with Cheetah 6.0; [g] Calculated detonation pressures with Cheetah 6.0; [h] Decompose before melting.

Table 2. Physical properties of iodide compounds (thermodynamic properties to be determined).

Compd	Structure	T_m [a] (°C)	T_d [b] (°C)	d [c] (g/cm³)	ΔH_f° [d] (kJ/mol)	ΔH_f° (kJ/g)	OB [e] (%)	D [f] (m/s)	P [g] (Gpa)	% Iodine
2b		-	236.0	3.33			-17.2			90.91
3b		-	270.3	3.28			-23.1			87.86
4b		138.6	254.9	2.67			-33.4			83.70
5b		120.0	230.3	3.21			-22.3			88.44

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ID	Structure	mp [a]	Tdec [b]	ρ [c]	[d]	[e]	[f]	[g]	
7b	(CH₃)(H₂N)N⁺–NH₂ · I₃⁻	–	111.2	2.54			–26.3		83.34
8b	(CH₃)₂N⁺–NH₂ · I₃⁻	86.9	194.8	2.74			–35.1		83.52
9c	[(CH₃)₂N⁺–CH₂–N⁺(CH₃)₂] · I₈²⁻	131.3	138.4	3.22			–27.9		88.47
10b	[(CH₃)₂N⁺–CH₂CH₂–N⁺(CH₃)₂] · 2 I₃⁻	191.8	221.7	2.88			–42.3		83.89
10c	[(CH₃)₂N⁺–CH₂CH₂–N⁺(CH₃)₂] · I₈²⁻	146.9	214.3	2.95			–31.7		87.41
11b	[(CH₃)₂N⁺–CH₂CH₂CH₂–N⁺(CH₃)₂] · 2 I₃⁻	207.5	274.9	2.75			–46.9		82.61
11c	[(CH₃)₂N⁺–CH₂CH₂CH₂–N⁺(CH₃)₂] · 2 I₅⁻	142.4	178.4	3.10			–28.0		88.79
TNT	–	h	295	1.65	–67	–0.3	–31.7	6881	19.53	–

[a] Melting point; [b] Decomposition temperature; [c] Density, measured by gas pycnometer (25 °C); [d] Heat of formation calculated with Gaussian 03; [e] Oxygen Balances. [f] Calculated detonation velocities with Cheetah 6.0; [g] Calculated detonation pressures with Cheetah 6.0; [h] Decompose before melting.

General Method for preparing iodide salts: For iodide salts **1a – 6a**, the corresponding amines **1 – 6** were reacted with stoichiometric amounts of HI in ethanol at room temperature. The precipitate formed was collected by filtration, washed with cold

ethanol, and dried under vacuum. Compounds **8a – 11a** were prepared by quaternization of amines **8 – 11** in ethanol with iodomethane in stoichiometric amounts.

1a: white plate shape crystals, yield: 80%. M.p.: 332 °C, T_{dec}: 336.6 °C. ^{1}H NMR: 7.78 (6H, s, NH$_3$) ppm, 3.03 (4H, s, CH$_2$) ppm; ^{13}C NMR: 36.33 ppm; IR (KBr): 3138, 2998, 2913, 1556, 1491, 1348, 1310, 1026, 997, 789 cm^{-1}.

2a: white solid, yield: 73%. M.p.: 257.1 °C, T_{dec}: 307.2 °C. ^{1}H NMR: 7.70 ppm (6H, s, NH); 2.88 ppm (4H, s, CH$_2$), 1.81 ppm (2H, t, CH$_2$); ^{13}C NMR: 36.2 ppm, 25.0 ppm; IR (KBr): 3040, 2992, 2753, 2386, 1954, 1582, 1460, 1400, 1207, 1177, 1153, 1090, 934, 768, 436 cm^{-1}.

3a: white solid, yield: 76%. M.p.: 240.5 °C, T_{dec}: 295.2 °C, ^{1}H NMR: 4.35 (6H, s, NH$_3$); 2. 71 (2H, t, CH$_2$); 2.60 (2H, t, CH$_2$) ppm; ^{13}C NMR: 48.64 ppm, 39.84 ppm; IR (KBr) 3242, 3100, 3055, 1555, 1474, 1335, 1295, 1217, 1121, 1057, 1005, 965, 887, 864, 836, 768, 486 cm^{-1}.

4a: white solid, yield: 64%. M.p.: 192.3 °C , T_{dec}: 318.2 °C. ^{1}H NMR: 5.4 ppm (6H, br, NH$_3$), 2.91 ppm (4H, t, CH$_2$), 2.60 ppm (4H, t, CH$_2$); ^{13}C NMR: 50.51 ppm, 36.51; IR (KBr): 3042, 2932, 1574, 1484, 1314, 1288, 1194, 1053, 992, 877, 807, 530, 501cm^{-1}.

5a: white solid, yield: 81%. M.p.: 332.8 °C, T_{dec}: 336.6 °C. ^{1}H NMR: 7.53 ppm (9H, s, NH$_3$), 2.93 ppm (6H, s, CH$_2$), 2.62 ppm (6H, s, CH$_2$) ; ^{13}C NMR: 50.31 ppm, 36.4 ppm; IR (KBr): 3401, 1574, 1448, 1125, 1080, 1051, 1007, 939, 770, 529 cm^{-1}. Anal. calcd for C$_6$H$_{21}$N$_4$I$_3$: C 13.60, H 3.99, N 10.57; found: C 13.40, H 3.82, N 10.07.

6a: white solid, yield: 82%. M.p.: 303.2 °C , T_{dec}: 342.0 °C. ^{1}H NMR: 8.02 (12H, s, NH$_2$) ppm, 3.11 (6H, s, CH$_2$) ppm; ^{13}C NMR: 38.8 ppm, 38.0 ppm; IR (KBr): 2982, 2904, 1572, 1487, 1396, 1346, 1264, 1193, 1036, 966, 942, 812, 540 cm^{-1}. Anal. calcd for C$_5$H$_{20}$N$_4$I$_4$: C 9.33, H 3.13, N 8.70; found: C 10.09, H 3.03, N 8.60.

7a: white solid, yield: 57%. M.p.: 133.0 °C, T_{dec}: 176.0 °C. ^{1}H NMR: 6.30 (4H, s, NH$_2$) ppm, 3.43 (6H, s, CH$_3$) ppm; 13C NMR: 60.1 ppm; IR (KBr): 3262, 3202, 3136,

3039, 3024, 2951, 1620, 1460, 1410, 1383, 1283, 1151, 1077, 957, 916, 839, 737, 504, 474 cm^{-1}. Anal. calcd for $C_2H_{10}N_3I$: C 11.83, H 4.96, N 20.70; found: C 11.99, H 4.88, N 19.72.

8a: white solid, yield: 95%. T_{dec}: 239.5 °C. ^{1}H NMR: 6.05 (2H, br, NH$_2$) ppm, 3.25 (9H, s, CH$_3$) ppm; ^{13}C NMR: 57.3 ppm; IR (KBr): 3289, 3232, 3149, 3015, 2938, 1605, 1474, 1432, 1394, 1281, 1142, 1055, 941, 895, 743, 477 cm^{-1}. Anal. calcd for $C_3H_{11}N_2I$: C 17.83, H 5.49, N 13.87; found: C 17.71, H 5.36, N 13.35.

9a: white solid, yield: 58%. M.p.: 316.0 °C. ^{1}H NMR: 4.63 ppm (2H, s, CH$_2$), 3.10 (18H, s, CH$_3$); ^{13}C NMR: 54.4 ppm, 48.7 ppm; IR (KBr): 3009, 2947, 1481, 1397, 1288, 1248, 1159, 1109, 945, 868, 454 cm^{-1}.

10a: white solid, yield: 52%. M.p.: 274.5 T_{dec}: 278.7 °C. ^{1}H NMR: 3.87 ppm (4H, s, CH$_2$), 3.16 (18H, s, CH$_3$); ^{13}C NMR: 57.1 ppm, 53.0 ppm; IR (KBr): 3004, 2970, 1630, 1488, 1472, 1448, 1403, 1219, 1129, 951, 920, 814, 745, 451 cm^{-1}.

11a: white solid, yield: 59%. M.p.: 304.8 °C. ^{1}H NMR: 3.35 ppm (4H,s, CH$_2$), 3.14 ppm (18H, s, CH$_3$), 2.22 ppm (2H, m, CH$_3$) ; ^{13}C NMR: 61.7 ppm, 52.6 ppm, 17.2 ppm; IR (KBr): 3445, 3007, 2957, 1622, 1476, 1402, 1242, 1055, 972, 944, 901, 761, 544 cm^{-1}.

General Method for preparing polyiodide salts: For polyiodide salts, an iodide compound was mixed with elemental iodine in stoichiometric amounts in ethanol; the mixture was stirred between 50 - 60 °C until all the solvent was evaporated. The solid residue was dried under vacuum at 50 °C overnight to obtain the corresponding polyiodide.

2b: black solid, yield: 93%. T_{dec}: 236.0 °C. IR (KBr): 3118, 1591, 1483, 1182, 1101, 926, 741, 569, 436 cm^{-1}. Anal. calcd for $C_3H_{12}N_2I_6$: C 4.30, H 1.44, N 3.34; found: C 4.38, H 1.52, N 3.21.

3b: black solid, yield: 95%. T_{dec}: 270.3 °C, IR (KBr) 3088, 1541, 1450, 1388, 1346, 1172, 1118, 1068, 993, 750, 514 cm^{-1}. Anal. calcd for $C_4H_{15}N_3I_6$: C 5.54, H 1.74, N 4.85; found: C 5.70, H 1.66, N 4.34.

4b: black solid, yield: 89%. M.p.: 138.6 °C, T_{dec}: 254.9 °C. IR (KBr): 3036, 1574, 1535 1447, 1346, 1292, 1130, 1076, 1000, 939, 871, 772, 755, 528, 500 cm^{-1}. Anal. calcd for $C_6H_{20}N_4I_6$: C 7.92, H 2.22, N 6.16; found: C 7.84, H 2.18, N 5.54.

5b: black solid, yield: 91%. M.p.: 120.0 °C, T_{dec}: 230.3 °C. IR (KBr): 3102, 1566, 1499, 1460, 1433, 1292, 1080, 1047, 1011, 980, 907, 889, 784, 769, 567, 534 cm^{-1}. Anal. calcd for $C_6H_{21}N_4I_9$: C 5.58, H 1.64, N 4.34; found: C 5.87, H 1.66, N 4.31.

7b: black solid, yield: 87%. T_{dec}: 111.2 °C. IR (KBr): 3147, 1700, 1629, 1401, 1016, 616 cm^{-1}. Anal. calcd for $C_2H_{10}N_3I_3$: C 5.26, H 2.21, N 9.20; found: C 5.29, H 2.27, N 8.85.

8b: black solid, yield: 94%. M.p. 86.9 °C, T_{dec}: 194.8 °C. IR (KBr): 3273, 3232, 3155, 3024, 1606, 1469, 1453, 1442, 1403, 1277, 1247, 1142, 1072, 942, 909, 742, 482 cm^{-1}. Anal. calcd for $C_3H_{11}N_2I_3$: C 7.90, H 2.43, N 6.15; found: C 8.02, H 2.29, N 5.92.

10b: black solid, yield: 85%. M.p.: 191.8 °C T_{dec}: 221.7 °C. IR (KBr): 3019, 2988, 1473, 1466, 1456, 1432, 1407, 951, 917, 793, 455 cm^{-1}. Anal. calcd for $C_8H_{22}N_2I_6$: C 10.59, H 2.44, N 3.09; found: C 10.74, H 2.28, N 2.94. Anal. calcd for $C_8H_{22}N_2I_6$: C 10.59, H 2.44, N 3.09; found: C 10.74, H 2.28, N 2.94.

11b: orange solid, yield: 89%. M.p.: 207.5 °C, T_{dec}: 274.9 °C. IR (KBr): 3463, 3013, 1481, 1466, 1445, 1412, 1403, 1269, 1242, 1140, 970, 941, 895, 764, 454 cm^{-1}. Anal. calcd for $C_9H_{24}N_2I_6$: C 11.73, H 2.62, N 3.04; found: C 11.77, H 2.44, N 2.99.

9c: black solid, yield: 81%. M.p.: 131.3 °C T_{dec}: 138.4 °C. Anal. calcd for $C_7H_{20}N_2I_8$: C 7.33, H 1.76, N 2.44; found: C 7.32, H 1.66, N 2.05.

10c: black solid, yield: 85%. M.p.: 146.9 °C T_{dec}: 214.3 °C. IR (KBr): 3014, 2754, 1472, 1159, 1113, 983, 945 cm^{-1}. Anal. calcd for $C_8H_{22}N_2I_8$: C 8.27, H 1.91, N 2.41; found: C 8.33, H 1.91, N 2.41.

11c: black solid, yield: 84%. M.p.: 142.4 °C, T_{dec}: 178.4 °C. IR (KBr): 3018, 1477, 1464, 1410, 1271, 1241, 1139, 1053, 970, 899, 760, 456 cm^{-1}. Anal. calcd for $C_9H_{24}N_2I_{10}$: C 7.56, H 1.69, N 1.96; found: C 7.70, H 1.54, N 1.96.

Table 3. Crystal data and structure refinement for **11b**.

Empirical formula	$C_9H_{24}I_6N_2$
Formula weight	921.7
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/m$
Unit cell dimensions	a = 9.489(2) Å α= 90°.
	b = 7.7651(18) Å β= 93.680(3)°
	c = 14.913(3) Å γ = 90°.
Volume	1096.6(4) Å^3
Z	2
Density (-123ºC)	2.791 Mg/m^3
Density (20ºC)	2.724 Mg/m^3
Absorption coefficient	8.488 mm^{-1}
F(000)	820
Crystal size	0.21 x 0.06 x 0.01 mm^3
Theta range for data collection	2.15 to 26.37°.
Index ranges	-11<=h<=11, -9<=k<=9, -17<=l<=18
Reflections collected	9382
Independent reflections	2409 [R_{int} = 0.0454]
Completeness to theta = 26.37°	99.80%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.920 and 0.550
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2409 / 0 / 118
Goodness-of-fit on F^2	0.981
Final R indices [I>2sigma(I)]	R_1 = 0.0317, wR_2 = 0.0716
R indices (all data)	R_1 = 0.0443, wR_2 = 0.0776
Largest diff. peak and hole	1.018 and -1.782 e.Å^{-3}

APPENDIX C

Alkyl ammonium cation stabilized biocidal polyiodides with adaptable high density and low pressure.

Abstract: The effective application of biocidal species requires building the active moiety into a molecular back bone that can be delivered and decomposed on demand under conditions of low pressure and prolonged high temperature detonation. The goal is to destroy storage facilities and their contents while utilizing the biocidal products arising from the released energy to destroy any remaining harmful airborne agents. Decomposition of carefully selected iodine-rich compounds can produce large amounts of the very active biocides, hydroiodic acid (HI) and iodine (I_2). Polyiodide anions, viz., I_3^-, I_5^-, which are excellent sources of such biocides, can be stabilized through interactions with large, symmetric cations such as alkyl ammonium salts. We have designed and synthesized suitable compounds of adaptable high density up to 3.33 g/cm^3, that are low pressure polyiodides with various alkyl ammonium cations whose deliverable iodine contents range between 58.0–90.9%.

Introduction

Interest in polyhalides has continued to expand due to their fascinating structural chemistry, and also because of their wide range of applications in the fields of semiconductors, superconductors, solar cells, optical devices, porous materials, etc.[1] The existence of halogen bonding interactions in the molecules helps to stabilize the formation of interesting structures. The triiodide anion, which has been known for almost two centuries, is the most stable polyhalide.[2] Recently, the adaptable properties for polyiodide compounds with alkyl cations were reported;[1b] studies also showed that the decomposition of iodine-rich compounds lead to large amounts of hydroiodic acid (HI) and iodine (I_2) both of which exhibit strong biocidal activity against biological agents, such as bacteria, fungi and yeasts, viruses, spores, and protozoan parasites.[3] Several iodine-rich compounds which generate high percentages of strong biocidesexhibit great potential as ingredients for Agent Defeat Weapons (ADWs) have been reported by our group (Figure 1).[3b]
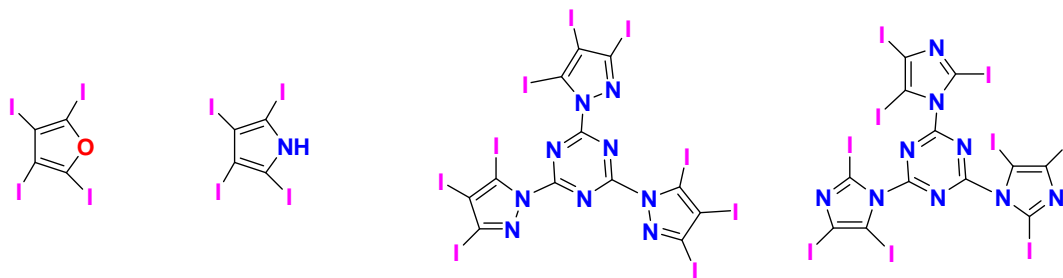
Figure 1 Potential ingredients for ADWs

Polyiodide salts exhibit low or no vapor pressures, have high densities, and high iodine content; furthermore, these materials have been shown to be very effective against pathogenic organisms in real life situations particularly as chemical agents that are effective in killing, e.g., viruses, bacteria and eukaryotic parasites.[4] However, there are a only a few polyiodide salts with heterocyclic cations, such as urotropinium triiodide,[5] bipyridinium triiodide, bipyridinium pentaiodide, and bipyridinium heptaiodide[6] that have calculated densities of 2.73, 2.50, 2.95 and 3.37 g/cm^3 (X-ray), respectively (Figure 2). The more interesting and more energetic urotropinium triiodide, unfortunately, is not very stable thermally, decomposing at 129 °C.[5]
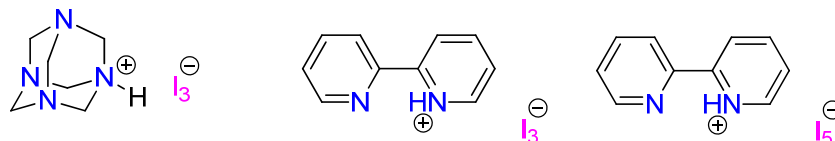
Figure 2 Polyiodides with N-heterocyclic cations

In general, the thermal stability of polyiodides can be enhanced by both increasing the size and the symmetry of the cation.[1e] Alkyl ammonium cations such as N, N-dimethylhydrazinium,[7] 2,2-dimethyltriazanium,[8] and some quaternized ammonium cation-based ionic liquids[9] (with appropriate anions) were shown to be hypergolic. Those N-containing alkyl cations may help to increase the energy and also result in low pressure when combining with polyiodide anions. It is well known that alkyl substituents reduce energy while concomitantly enhancing stability. The alkyl ammonium polyiodides should be ideal materials to generate low pressure detonations as well as to result in effective biocidal decomposition products. We believe that polyiodide compounds have not been studied as ingredients in ADWs. Based on our continuing interest in seeking effective materials for bio-agent destruction, we synthesized and characterized compounds of adaptable high-density, low pressure polyiodides with various alkyl ammonium cations and iodine percentages ranging from 58.0 – 90.9%.

Results and Discussion

The strongly basic properties of aliphatic amines allow them to react easily with hydrogen iodide (HI) to form the corresponding iodide salts. The reaction of alkyl dimethylamine with methyl iodide should result in the formation of the N,N,N-trimethylammonium cation which could stabilize the polyiodide anion. However, the longer carbon chain and the formation of this cation would also decrease the oxygen balance dramatically. In order to explore the properties of such polyiodide salts, amines **1 - 11** were selected as starting materials. The iodide salts **1a–6a** and **8a –11a** were prepared from the corresponding amine with HI or iodomethane by controlling the stoichiometry of the reaction. All of the iodide salts precipitated from ethanol solvent and were collected by filtration and washed with cold ethanol and dried under vacuum. Compound **7a** was prepared according to the literature from the corresponding chloride as shown in Scheme 2.[8] With the pure iodide salts in hand, the corresponding triiodide salts, **1b–8b,** were prepared by reacting the iodides with stoichiometric amounts of elemental iodine in ethanol, while triiodides, **9b–11b,** were obtained in acetone in good

yields and purities after removing acetone. However, a mixture of triiodide (**2b–5b, 7b–8b**) salts and the iodide starting materials were obtained likely arising from the poor solubility of the iodides in ethanol solution. When the reaction mixture in ethanol was heated at 50 °C and the solvent was allowed to evaporate slowly to dryness, black triiodide salts (**2b–5b, 7b–8b**) were obtained in essentially excellent yields and pure enough to pass elemental analyses. Failure to obtain **1b** and **6b**, with only the starting materials, **1a** and **6a,** being recovered, may be due to their poor solubility in alcohol or that the products were unstable under the conditions tried (Schemes 1 and 2).

Scheme 1 Preparation of alkyl ammonium iodide and triiodide

Scheme 2 Synthesis of quaternary ammonium iodides and polyiodides.

In a similar manner, when **2a–5a, 7a** and **8a** were reacted with additional two or more equivalents of elemental iodine, only the corresponding triiodide salts rather than any higher polyiodide salts were recovered. This may arise from the small size of the cations which may be incapable of stabilizing the anticipated higher polyiodides. However, the di-pentaiodide, **10c,** and tri-pentaiodide, **11c,** salts were prepared successfully perhaps benefiting from the stabilizing effect of the larger cations. Interestingly, in the case of **9a**, the anion was found to be I_8^{2-} (confirmed by elemental analyses) rather than the di-pentaiodide (Scheme 2). All the compounds obtained were characterized by IR, DSC and elemental analysis. The same values for ^1H and ^{13}C NMR chemical shifts in a common cation were found in the iodide and in the polyiodide salts. The structure of **10b** was further confirmed by X-ray single crystal diffraction.

A suitable crystal of **10b** for X-ray analysis was grown from acetone. Salt **10b** crystallizes in the monoclinic space group $P2_1/m$; the crystal data and structure refinement details are given in Table 1, and the crystal structure is shown in Figure 3. The I - I bond distances for I_1-I_2, I_2-I_3, I_4-I_5 and I_5-I_6 are 2.8557(9), 2.9809(9), 2.9202(9) and 2.9116(9) Å, respectively, which are much shorter than the VDW distance (4.3 Å). The two linear triiodide anions [angles: I(1)-I(2)-I(3) = 178.06(3), I(6)-I(5)-I(4) = 174.78(3)] are located on both sides of the cation. The atoms of I1, I2, I3, I4, I5, I6, C7, N1, C2, C3, C4, N5 and C8 are coplanar; while the atoms of C6, C6A, C9, C9A are also located in another plane. Those two planes are perpendicular to each other.

Table 1. Crystal data and structure refinement for **10b**.

Empirical formula	$C_9H_{24}I_6N_2$
Formula weight	921.7
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/m$
Unit cell dimensions	a = 9.489(2) Å α= 90°.
	B = 7.7651(18) Å β= 93.680(3)°.
	C = 14.913(3) Å γ = 90°.
Volume	1096.6(4) Å^3
Z	2
Density (-123ºC)	2.791 Mg/m^3
Density (20ºC)	2.724 Mg/m^3
Absorption coefficient	8.488 mm^{-1}
F(000)	820
Crystal size	0.21 x 0.06 x 0.01 mm^3
Theta range for data collection	2.15 to 26.37°.
Index ranges	-11<=h<=11, -9<=k<=9, -17<=l<=18
Reflections collected	9382
Independent reflections	2409 [R_{int} = 0.0454]
Completeness to theta = 26.37°	99.80%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.920 and 0.550
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2409 / 0 / 118
Goodness-of-fit on F^2	0.981
Final R indices [I>2sigma(I)]	R_1 = 0.0317, Wr_2 = 0.0716
R indices (all data)	R_1 = 0.0443, Wr_2 = 0.0776
Largest diff. peak and hole	1.018 and -1.782 e.Å^{-3}
CCDC	983933
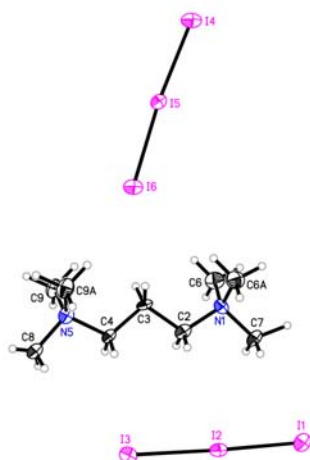
Figure 3 Crystal structure of **10b**

In the packing diagram of **10b**, the hydrogen bonds of I...H-C aid in the formation of 3-D network structure (Table 2). Twin columns of triiodide anions are pinned in position by the networks of I...H-C interactions with the heads of cations as is seen from the packing diagram viewed along the a-axis (Figure 4a). The two triiodide anions are packed in a T-shaped pattern with I-I interactions (I1-I5 = 3.898 Å) as shown in Figure 4b. Further details are provided in the ESI.

Table 2 Hydrogen bonds present in **10b**.

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C7-H7A...I3[i]	1.2400	2.7300	3.9105(9)	159.00

[i]: symmetrical operator codes : -x,-1/2+y,-z

a

b
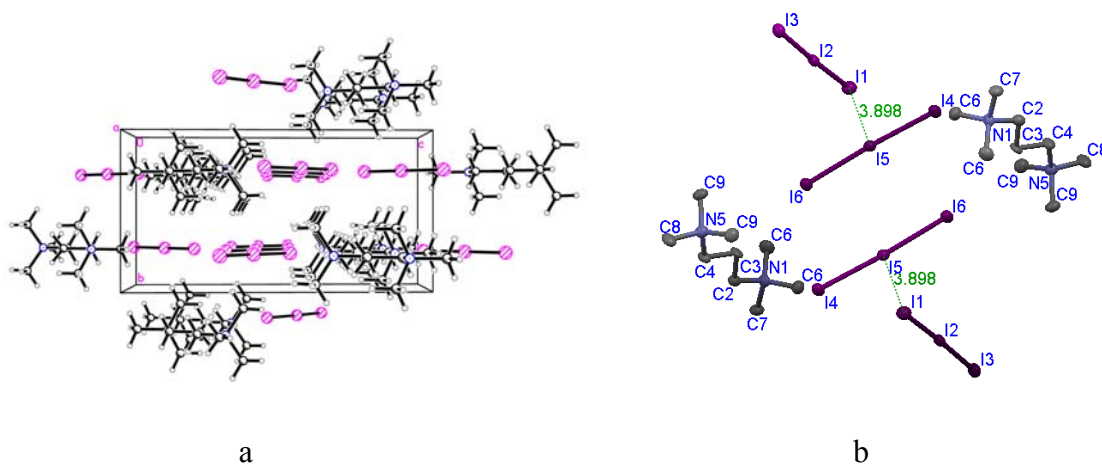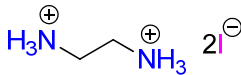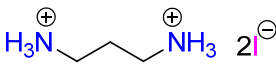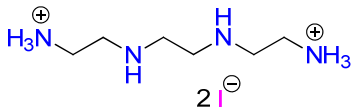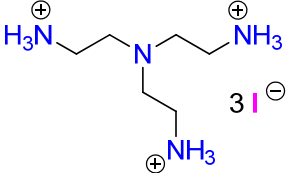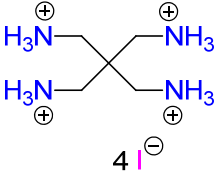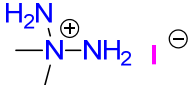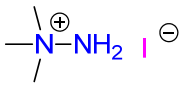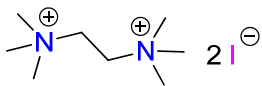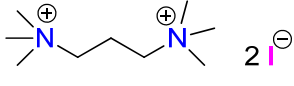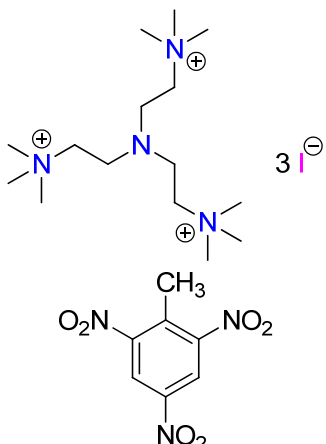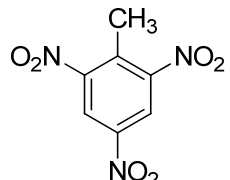
Figure 4 Packing diagram of **10b** (a) viewed from the a-axis; and (b) interactions between the two triiodide anions.

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The physical properties of all iodide and polyiodide compounds are listed in Tables 3 and 4. Most of the iodide compounds with the exception of **7a** and **7b** which decompose at 176.0 and 111.2 °C, respectively, have very good thermal stabilities The iodide salts, **1a–11a,** have an iodine content ranging from 60.70% (**11a**) to 80.34% (**1a**), while the polyiodide salts exhibit an iodine content from 82.25% (**11b**) to 90.91% (**2b**)(Table 5). An increase in iodine content destabilizes the corresponding polyiodides (**10a**>**10b**>**10c, 11a**>**11b**>**11c**).

The iodide compounds exhibit densities ranging from 1.73 g/cm^3 to 3.33 g/cm^3. The introduction of the polyiodide species results in an increase of density from 0.49 g/cm^3 to 1.35 g/cm^3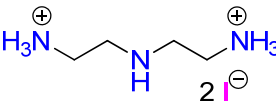 compared to the corresponding precursor iodide salt; furthermore, the formation of polyiodide also helps to improve the oxygen balance and iodine content. The impact sensitivity measurements were made using standard BAM techniques. All of the compounds were found to be impact insensitive (>40J). The heat of formation of the cations for salts **1-10** were calculated by employing Gaussian 03 (Revision D. 01) using the G2 method.[10,11] The heat of formation of the cation for salts **11a**, **11b** and **11c** was calculated via an isodesmic reaction (ESI),[12] and those of the iodide, triiodide, and pentaiodide anions were obtained from NIST.[13] The heats of formation for the salts can be obtained using Born–Haber energy cycles by using the lattice energy of the salts.[14] However, the heat of formation for salt **9c** could not be calculated due to the lack of availability of a value for the heat of formation for I_8^{2-}.

Table 3 Physical properties of iodide compounds
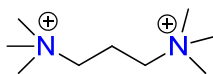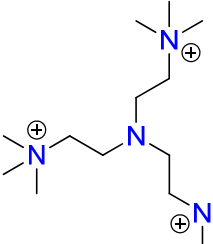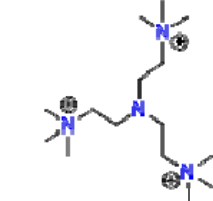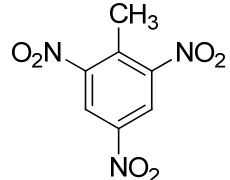
Compd	Structure	$T_m^{[a]}$ (°C)	$T_d^{[b]}$ (°C)	$d^{[c]}$ (g/cm^3)	$\Delta H_f^{\circ [d]}$ (kJ/mol)	ΔH_f° (kJ/g)	$OB^{[e]}$ (%)	$D^{[f]}$ (m/s)	$P^{[g]}$ (Gpa)
1a		332.8	335.5	2.75	-319.5	-1.01	-40.5	-	-
2a		257.1	-	2.52	-370.5	-1.12	-53.3	-	-
3a		240.5	-	2.34	-348.7	-0.97	-64.6	2375	0.94
4a		192.3	312.4	2.07	-337.7	-0.84	-63.6	3220	4.15

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Compound	[a]	[b]	[c]	[d]	[e]		[f]	[g]
5a	318.1	322.5	2.44	-288.2	-0.54	-63.4	3310	4.76
6a	303.2	342.2	2.46	53.3	0.08	-44.7	3370	6.58
7a	133.0	176.0	2.05	45.2	0.22	-67.0	4610	10.05
8a	h	238.8	1.84	-60.8	-0.30	-87.1	3920	6.58
9a	274.5	276.2	1.83	-278.1	-0.70	-104.0	3480	4.41
10a	304.8	-	1.73	-328.8	-0.79	-112.1	3400	4.00
11a	h	289.7	1.67	-180.9		-117.1	3900	5.70
TNT	h	295	1.65	-67	-0.3	-31.7	6881	19.53

[a] Melting point; [b] Decomposition temperature; [c] Density, measured by gas pycnometer (25 °C); [d] Heat of formation calculated with Gaussian 03; [e] Oxygen balance. [f] Calculated detonation velocity with Cheetah 6.0; [g] Calculated detonation pressure with Cheetah 6.0; [h] Decomposes before melting.

Table 4. Physical properties of polyiodide compounds

Compd	Structure	T_m[a] (°C)	T_d[b] (°C)	d [c] (g/cm³)	ΔH_f° [d] (kJ/mol)	ΔH_f° (kJ/g)	OB[e] (%)	D[f] (m/s)	P[g] (Gpa)
2b	H_3N^+–CH₂CH₂CH₂–NH_3^+ · 2 I_3^-	h	233.4	3.33	-188.8	-0.23	-17.2	1800	2.28
3b	H_3N^+–CH₂CH₂–NH–CH₂CH₂–NH_3^+ · 2 I_3^-	h	270.3	3.28	-217.8	-0.25	-23.1	2100	2.56
4b	H_3N^+–CH₂CH₂–NH–CH₂CH₂–NH–CH₂CH₂–NH_3^+ · 2 I_3^-	138.6	253.9	2.67	-216.8	-0.24	-33.4	2350	3.56
5b	tris(2-ammonioethyl)amine · 3 I_3^-	120.0	283.7	3.21	63.8	0.05	-22.3	2630	4.78
7b	H_2N–N$^+$(CH₃)–NH₂(NH₂) · I_3^-	h	111.2	2.54	46.4	0.10	-26.3	2900	4.96
8b	(CH₃)₂N$^+$H–NH₂ · I_3^-	86.9	194.8	2.74	-83.2	-0.18	-35.1	2670	4.40
9b	(CH₃)₃N$^+$–CH₂CH₂–N$^+$(CH₃)₃ · 2 I_3^-	191.8	220.8	2.88	-230.2	-0.25	-42.3	2620	3.63
9c	(CH₃)₃N$^+$–CH₂CH₂–N$^+$(CH₃)₃ · I_8^{2-}	146.9	214.0	2.95	-	-	-31.7	-	-
10b	(CH₃)₃N$^+$–CH₂CH₂CH₂–N$^+$(CH₃)₃ · 2 I_3^-	207.5	272.3	2.75	-294.2	-0.03	-46.9	2560	3.28

10c	(structure) $2\,I_5^-$	142.4	178.0	3.10	-182.0	-0.13	-28.0	2360	3.29
11b	(structure) $3\,I_3^-$	135.9	275.0	2.45	-30.9	-0.02	-50.8	2800	4.23
11c	(structure) $3\,I_4^-$	99.7	231.4	2.96	114.9	0.05	-30.8	2480	3.69
TNT	(structure)	h	295	1.65	-67	-0.3	-31.7	6881	19.53

[a] Melting point; [b] Decomposition temperature; [c] Density, measured by gas pycnometer (25 °C); [d] Heat of formation calculated with Gaussian 03; [e] Oxygen balance. [f] Calculated detonation velocity with Cheetah 6.0; [g] Calculated detonation pressure with Cheetah 6.0; [h] Decomposes before melting.

From the values of the heats of formation and experimental densities, the detonation pressures (P) and velocities (D) were calculated using CHEETAH 6.0 in exhaust condition as listed in Tables 3 and 4. The detonation properties of **1a** and **2a** could not be obtained due to the non-convergence of the calculation. All the compounds exhibit low detonation pressures ranging from 0.94 to 10.05 GPa and velocities from 1800 to 4610 m/s. The increasing number of N-NH$_2$ moieties and the number of nitrogen atoms present in the molecule results in increasing detonation velocity and pressure; while the formation of polyiodide decreases the detonation pressure resulting in the desired low pressure. Therefore, the energy and iodine content for the polyiodide can be adapted and controlled by choosing suitable cations in collaboration with the anions of iodide, triiodide, or pentaiodide to achieve the appropriate iodine content.

Decomposition products

The decomposition products were calculated via CHEETAH 6.0 by arbitrarily assuming the conditions of 1 atm at 298K. The major products are listed in Table 5 in units of weight-%. By comparing the iodine content (column 9) with the sum of I$_2$ and HI in the products (column 10), it can be easily concluded that the anions in the salts were

completely decomposed to I_2 and HI; in most cases with the value of $\Sigma(I_2+HI)$ equal or slightly higher than that of % iodine due to the formation of HI. For **6a**, **7a**, **8a**, **5b**, **7b**, slightly lower $\Sigma(I_2+HI)$ values were obtained because of the formation of CH_3I as a product. The high percentage of effective biocides in the products endows these compounds with great potential as an ingredient for ADWs.

Table 5. Major decomposition products of polyiodide salts (in weight %, kg/kg)

compd	N_2 (g)	I_2 (g)	HI (g)	CH_3I	C (s)	CH_4 (g)	NH_3 (g)	% Iodine	$\Sigma(I_2+HI)/$ (%)
1a	8.10	21.88	58.92	-	-	10.16	0.94	80.34	80.8
2a	8.49	75.36	1.58	-	-	14.54	-	76.92	76.94
3a	11.71	69.10	1.61	-	0.87	16.71	-	70.70	70.71
4a	-	63.08	0.05	-	10.26	3.43	16.94	63.13	63.13
5a	10.71	70.26	1.59	-	1.74	15.84		71.84	71.85
6a	2.69	51.65	26.48	0.76	3.86	4.38	7.31	78.84	78.13
7a	4.27	38.74	23.19	0.75	7.56	3.07	19.97	62.51	61.93
8a	1.91	44.97	17.59	0.42	8.56	7.64	14.54	62.81	62.56
9a	7.02	61.78	1.67	-	7.54	22.00	-	63.44	63.45
10a	6.77	59.63	1.67	-	8.74	23.19	-	61.29	61.3
11a	8.54	56.38	1.65	-	9.65	23.78	-	58.02	58.03
2b	0.48	90.77	0.14	-	1.81	3.16	3.48	90.91	90.91
3b	4.85	86.63	1.25	-	0.38	6.90	-	87.86	87.88
4b	6.16	82.37	1.34	-	1.35	8.78	-	83.70	83.71
5b	1.47	70.48	17.57	0.25	2.69	2.61	3.49	88.44	88.05
7b	6.19	53.69	28.77	0.82	0.99	4.22		83.34	82.46
8b	6.14	82.14	1.38	-	0.69	9.64	-	83.52	83.52
9b	3.09	82.54	1.37	-	3.34	9.68	-	83.89	83.91
10b	3.04	81.24	1.38	-	3.94	10.40	-	82.61	82.62
10c	2.15	86.46	1.24	-	2.80	7.35	-	88.79	87.70
11b	3.95	79.17	1.40	-	4.48	10.99	-	80.57	80.57
11c	2.57	86.14	1.23	-	2.92	7.14	-	87.36	87.37

Conclusions

A series of polyiodide compounds with adaptable high-density, low-pressure properties were synthesized, characterized, and evaluated. The energies of the compounds are dominated by the cations; more N-NH$_2$ moieties and nitrogen atoms would improve the detonation properties. The densities of the compounds are determined by the anion; a 0.49 g/cm^3 to 1.35 g/cm^3 density increase was obtained by the formation of polyiodide (triiodide and pentaiodide). The anions in these new salts are converted nearly completely to effective biocides which make them ideal candidates for ingredients used in ADWs.

Experimental Section

General Methods: The commercially available amines **1**–**5**, **7**–**10**, reagents from Alfa-Aesar and Acros Organics, were used as received. Amines **6**[15] and **11**[16] were prepared according to the literature. ^{1}H and ^{13}C NMR spectra were recorded on a 300 MHz (Bruker AVANCE 300) nuclear magnetic resonance spectrometer operating at 300 and 75.48 MHz, respectively, by using DMSO-d$_6$ as solvent and locking solvent unless otherwise stated. The melting and decomposition (onset) temperatures were obtained on a differential scanning calorimeter (TA Instruments Co., model Q10) at a scan rate of 5 °C min^{-1}. IR spectra were recorded using KBr pellets for solids on a BIORAD model 3000 FTS spectrometer. Densities of the polyiodide compounds were measured at 25 °C by employing a Micromeritics AccuPyc 1330 gas pycnometer. Elemental analyses were obtained by using an Exeter CE-440 elemental analyzer.

X-ray analyses: A purple plate of dimensions 0.21 x 0.06 x 0.01 mm^3 was mounted on a MiteGen MicroMesh using a small amount of Cargille Immersion Oil. Data were collected on a Bruker three-circle platform diffractometer equipped with a SMART APEX II/Platinum 135 CCD detector. The crystals were irradiated using graphite monochromated MoK$_\alpha$ radiation (λ = 0.71073). An Oxford Cobra low temperature device was used to maintain the crystals at a constant 150(2) K during data collection. Data collection was performed and the unit cell was initially refined using APEX2 [v2010.3-0].[17] Data reduction was carried out using SAINT [v7.68A][18] and XPREP [v2008/2].[19] Corrections were applied for Lorentz, polarization, and absorption effects using SADABS [v2008/1].[20] The structure was solved and refined with the aid of the programs in the SHELXTL-plus [v2008/4] system of programs.[21] The full-matrix least-squares refinement on F2 included atomic coordinates and anisotropic thermal parameters for all non-H atoms. The H atoms were included using a riding model.

General Method for preparing iodide salts: For iodide salts **1a** − **6a**, the corresponding amines **1** − **6** were reacted with stoichiometric amounts of HI in ethanol solvent at room temperature. The precipitate formed was collected by filtration, washed with cold ethanol, and dried under vacuum. Compound **7a** was prepared using a similar method in the literature.[8] Salts **8a**–**11a** were preparing by quaternization of amines **8**–**11** in ethanol with iodomethane in stoichiometric quantities.

1a:[22] White plate shaped crystals, yield: 80%. M.p.: 332.8 °C; T_{dec} (onset): 335.5 °C. ^{1}H NMR: 7.78 (6H, s, NH$_3$) ppm, 3.03 (4H, s, CH$_2$) ppm; ^{13}C NMR: 36.33 ppm; IR (KBr): 3138, 2998, 2913, 1556, 1491, 1348, 1310, 1026, 997, 789 cm^{-1}.

2a:[23] White solid, yield: 73%. M.p.: 257.1 °C. ^{1}H NMR: 7.70 ppm (6H, s, NH); 2.88 ppm (4H, s, CH$_2$), 1.81 ppm (2H, t, CH$_2$); ^{13}C NMR: 36.2 ppm, 25.0 ppm; IR (KBr): 3040, 2992, 2753, 2386, 1954, 1582, 1460, 1400, 1207, 1177, 1153, 1090, 934, 768, 436 cm^{-1}.

3a:[24] White solid, yield: 76%. M.p.: 240.5 °C. ^{1}H NMR: 4.35 (6H, s, NH$_3$); 2.71 (2H, t, CH$_2$); 2.60 (2H, t, CH$_2$) ppm; ^{13}C NMR: 48.64 ppm, 39.84 ppm; IR (KBr) 3242, 3100, 3055, 1555, 1474, 1335, 1295, 1217, 1121, 1057, 1005, 965, 887, 864, 836, 768, 486 cm^{-1}.

4a:[24] White solid, yield: 64%. M.p.: 192.3 °C; T_{dec} (onset): 312.4 °C. ^{1}H NMR: 5.4 ppm (6H, br, NH$_3$), 2.91 ppm (4H, t, CH$_2$), 2.60 ppm (4H, t, CH$_2$); ^{13}C NMR: 50.51 ppm, 36.51; IR (KBr): 3042, 2932, 1574, 1484, 1314, 1288, 1194, 1053, 992, 877, 807, 530, 501cm^{-1}.

5a:[24] White solid, yield: 81%. M.p.: 318.1 °C; T_{dec} (onset): 322.5 °C. ^{1}H NMR: 7.53 ppm (9H, s, NH$_3$), 2.93 ppm (6H, s, CH$_2$), 2.62 ppm (6H, s, CH$_2$) ; ^{13}C NMR: 50.31 ppm, 36.4 ppm; IR (KBr): 3401, 1574, 1448, 1125, 1080, 1051, 1007, 939, 770, 529 cm^{-1}. Anal. calcd for C$_6$H$_{21}$N$_4$I$_3$: C 13.60, H 3.99, N 10.57; found: C 13.40, H 3.82, N 10.07.

6a: White solid, yield: 82%. M.p.: 303.2 °C; T_{dec} (onset): 342.2 °C. ^{1}H NMR: 8.02 (12H, s, NH$_2$) ppm, 3.11 (6H, s, CH$_2$) ppm; ^{13}C NMR: 38.8 ppm, 38.0 ppm; IR (KBr): 2982, 2904, 1572, 1487, 1396, 1346, 1264, 1193, 1036, 966, 942, 812, 540 cm^{-1}. Anal. calcd for C$_5$H$_{20}$N$_4$I$_4$: C 9.33, H 3.13, N 8.70; found: C 10.09, H 3.03, N 8.60.

7a:[8] White solid, yield: 57%. M.p.: 133.0 °C, T_{dec} (onset): 176.0 °C. ^{1}H NMR: 6.30 (4H, s, NH$_2$) ppm, 3.43 (6H, s, CH3) ppm; ^{13}C NMR: 60.1 ppm; IR (KBr): 3262, 3202, 3136, 3039, 3024, 2951, 1620, 1460, 1410, 1383, 1283, 1151, 1077, 957, 916, 839, 737, 504, 474 cm^{-1}. Anal. calcd for C$_2$H$_{10}$N$_3$I: C 11.83, H 4.96, N 20.70; found: C 11.99, H 4.88, N 19.72.

8a: White solid, yield: 95%. T_{dec} (onset): 238.8 °C. ^{1}H NMR: 6.05 (2H, br, NH$_2$) ppm, 3.25 (9H, s, CH3) ppm; ^{13}C NMR: 57.3 ppm; IR (KBr): 3289, 3232, 3149, 3015, 2938, 1605, 1474, 1432, 1394, 1281, 1142, 1055, 941, 895, 743, 477 cm^{-1}. Anal. calcd for C$_3$H$_{11}$N$_2$I: C 17.83, H 5.49, N 13.87; found: C 17.71, H 5.36, N 13.35.

9a:[25] White solid, yield: 52%. M.p.: 274.5 ºC; T_{dec} (onset): 276.2 °C. ^{1}H NMR: 3.87 ppm (4H, s, CH$_2$), 3.16 (18H, s, CH3); ^{13}C NMR: 57.1 ppm, 53.0 ppm; IR (KBr): 3004, 2970, 1630, 1488, 1472, 1448, 1403, 1219, 1129, 951, 920, 814, 745, 451 cm^{-1}.

10a:[25] White solid, yield: 59%. M.p.: 304.8 °C. ^{1}H NMR: 3.35 ppm (4H, s, CH$_2$), 3.14 ppm (18H, s, CH3), 2.22 ppm (2H, m, CH3) ; ^{13}C NMR: 61.7 ppm, 52.6 ppm, 17.2 ppm; IR (KBr): 3445, 3007, 2957, 1622, 1476, 1402, 1242, 1055, 972, 944, 901, 761, 544 cm^{-1}.

11a:[16] White solid, yield: 63%. T_{dec} (onset): 289.7 °C. ^{1}H NMR: 3.57 ppm (6H, m, CH$_2$), 3.17 ppm (27H, s, CH$_3$), 3.00 ppm (6H, m, CH$_2$); ^{13}C NMR: 61.3 ppm, 52.9 ppm, 46.2 ppm; IR (KBr): 3456, 3005, 2972, 1478, 1353, 1281, 1234, 1177, 1118, 1045, 967, 916, 866, 810, 795 cm^{-1}; Anal. calcd for C$_{15}$H$_{39}$N$_4$I$_3$: C 27.45, H 5.99, N 8.54; found: C 27.45, H 5.91, N 8.66.

General Method for preparing polyiodide salts: For polyiodide salts, the respective iodide compounds were mixed with elemental iodine in stoichiometric amounts in ethanol or acetone; the mixture was stirred at 50–60 °C until all the solvent had evaporated. The solid residue was dried under vacuum at 50 °C overnight to obtain the corresponding polyiodide.

2b: Black solid, yield: 93%. T_{dec} (onset): 233.4 °C. IR (KBr): 3118, 1591, 1483, 1182, 1101, 926, 741, 569, 436 cm^{-1}. Anal. calcd for C$_3$H$_{12}$N$_2$I$_6$: C 4.30, H 1.44, N 3.34; found: C 4.38, H 1.56, N 3.21.

3b: Black solid, yield: 95%. T_{dec} (onset): 270.3 °C. IR (KBr) 3088, 1541, 1450, 1388, 1346, 1172, 1118, 1068, 993, 750, 514 cm^{-1}. Anal. calcd for C$_4$H$_{15}$N$_3$I$_6$: C 5.54, H 1.74, N 4.85; found: C 5.70, H 1.66, N 4.34.

4b: Black solid, yield: 89%. M.p.: 138.6 °C; T_{dec} (onset): 253.9 °C. IR (KBr): 3036, 1574, 1535 1447, 1346, 1292, 1130, 1076, 1000, 939, 871, 772, 755, 528, 500 cm^{-1}. Anal. calcd for C$_6$H$_{20}$N$_4$I$_6$: C 7.92, H 2.22, N 6.16; found: C 7.84, H 2.18, N 5.54.

5b: Black solid, yield: 91%. M.p.: 120.0 °C; T_{dec} (onset): 283.7 °C. IR (KBr): 3102, 1566, 1499, 1460, 1433, 1292, 1080, 1047, 1011, 980, 907, 889, 784, 769, 567, 534 cm^{-1}. Anal. calcd for C$_6$H$_{21}$N$_4$I$_9$: C 5.58, H 1.64, N 4.34; found: C 5.87, H 1.66, N 4.31.

7b: Black, yield: 87%. T_{dec}(onset): 111.2 °C. IR (KBr): 3147, 1700, 1629, 1401, 1016, 616 cm^{-1}. Anal. calcd for C$_2$H$_{10}$N$_3$I$_3$: C 5.26, H 2.21, N 9.20; found: C 5.29, H 2.27, N 8.85.

8b: Black solid, yield: 94%. M.p.: 86.9 °C; T_{dec} (onset): 194.8 °C. IR (KBr): 3273, 3232, 3155, 3024, 1606, 1469, 1453, 1442, 1403, 1277, 1247, 1142, 1072, 942, 909, 742, 482 cm^{-1}. Anal. calcd for C$_3$H$_{11}$N$_2$I$_3$: C 7.90, H 2.43, N 6.15; found: C 8.02, H 2.29, N 5.92.

9b: Black solid, yield: 85%. M.p.: 191.8°C; T_{dec} (onset): 220.8 °C. IR (KBr): 3019, 2988, 1473, 1466, 1456, 1432, 1407, 951, 917, 793, 455 cm^{-1}. Anal. calcd for C$_8$H$_{22}$N$_2$I$_6$: C 10.59, H 2.44, N 3.09; found: C 10.74, H 2.28, N 2.94. Anal. calcd for C$_8$H$_{22}$N$_2$I$_6$: C 10.59, H 2.44, N 3.09; found: C 10.74, H 2.28, N 2.94.

10b: Orange solid, yield: 89%. M.p.: 207.5 °C; T_{dec} (onset): 272.3 °C. IR (KBr): 3463, 3013, 1481, 1466, 1445, 1412, 1403, 1269, 1242, 1140, 970, 941, 895, 764, 454 cm^{-1}. Anal. calcd for C$_9$H$_{24}$N$_2$I$_6$: C 11.73, H 2.62, N 3.04; found: C 11.77, H 2.44, N 2.99.

11b: Orange solid, yield: 92%. M.p.: 135.9 °C; T_{dec} (onset) : 275.0 °C; IR (KBr): 3452, 3013, 2951, 1470, 1442, 1416, 1231, 1173, 1109, 1038, 964, 946, 913, 793 cm^{-1}; Anal. calcd for C$_{15}$H$_{39}$N$_4$I$_9$: C 12.71, H 2.77, N 3.95; found: C 12.94, H 2.64, N 3.90.

9c: Black solid, yield: 85%. M.p.: 146.9 °C; T_{dec} (onset): 214.0 °C. IR (KBr): 3014, 2754, 1472, 1159, 1113, 983, 945 cm^{-1}. Anal. calcd for $C_8H_{22}N_2I_8$: C 8.27, H 1.91, N 2.41; found: C 8.33, H 1.78, N 2.35.

10c: Black solid, yield: 84%. M.p.: 142.4 °C; T_{dec} (onset) : 178.0 °C. IR (KBr): 3018, 1477, 1464, 1410, 1271, 1241, 1139, 1053, 970, 941, 899, 760, 456 cm^{-1}. Anal. calcd for $C_9H_{24}N_2I_{10}$: C 7.56, H 1.69, N 1.96; found: C 7.70, H 1.54, N 1.96.

11c: Black solid, yield: 90%. M.p.: 99.7 °C; T_{dec} (onset): 231.4 °C. IR (KBr): 3452, 3016, 1479, 1469, 1459, 1406, 1290, 1167, 1104, 961, 918, 861 cm^{-1}; Anal. calcd for $C_{15}H_{39}N_4I_{15}$: C 8.27, H 1.80, N 2.57; found: C 8.33, H 1.62, N 2.51.

Acknowledgements

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ix) APPENDIX D

Versatile Polyiodopyrazoles: Synthesis and Biocidal Promise

Chand, D. and Shreeve, J. M. *Chem. Commun.* **2015***, 51,* 3438-3441

An efficient route to polyiodopyrazoles, 3, 4, 5-triiodopyrazole   (**1**), 1-methyl-3, 4, 5-triiodopyrazole (**2**) and 1-diiodomethyl-3, 4, 5-triiodopyrazole (**3**), opens the door to prospective biocides. Nitration of 1 and 2 gives the previously inaccessible compounds, 3, 4-dinitro-5-iodopyrazole (**4**), and 3, 4-dinitro-5-iodo-1-methylpyrazole (**5**), respectively. These synthetic pathways will open many fronts for pyrazole chemistry.

Modern warfare is no longer limited to the use of conventional weapons; there is believed to be a huge store of chemical and biological weapons distributed among various countries as well as illegitimate groups around the world. As a result interest

in developing Agent Defeat Weapons (ADWs) has grown significantly during the last few years.[1] ADWs are airborne warheads which contain anti bioagent materials which may be iodine-rich compounds that form large amounts of elemental iodine, and hydroiodic acid (HI) as detonation products − strong biocides against such agents as viruses, spores, bacteria, and parasites.[2, 3] ADWs demand easily containable, non sublimable, and thermally stable sources of iodine or iodine-containing species (Figure 1).[3]

Various periodo heterocyclicarenes including tetraiodofuran (TIF) and 3, 4, 5-triiodopyrazole have been synthesized in our lab and studied systematically.[3a] They are being tested as effective antibioagent ingredients suitable for application as ADWs. Polyiodide salts which have low vapor pressure, high densities, and high iodine content also provide another opportunity to increase the iodine concentration in target compounds.[3b]
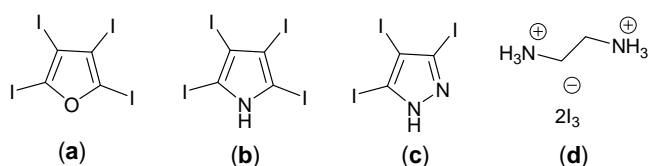

Figure 1: Possible ADWs - (a) Tetraiodofuran (TIF); (b) 2,3,4,5-Tetraiodo-1H pyrrole; (c) 3,4,5-Triiodo-1H-pyrazole; (d) Ethane-1,2-diammonium-bis(triiodide).

Current methods for the iodination of pyrazoles suffer from a variety of difficulties. Pyrazoles with electron donating substituents have been iodinated using iodine-iodide (I_2-KI) or iodine monochloride (ICl); both routes often use large quantities of reactants.[4] An iodine-aqueous ammonia combination gives a mixture of 3, 4-diiodo- and 3, 4, 5-triiodopyrazoles in very low yields.[5] Only diiodo derivatives were obtained when an oxidative iodination methodology – I_2-HIO_3 – was attempted.[6] Likely because of the lack of good synthetic routes, the chemistry and properties of polyiodopyrazoles have not been studied widely.

Now we report an efficient synthesis route for polyiodopyrazoles, viz., 3, 4, 5-triiodopyrazole (**1**), 1-methyl-3, 4, 5-triiodopyrazole (**2**) and 1-diiodomethyl-3, 4, 5-triiodopyrazole (**3**) in good to excellent yields. The introduction of the diiodomethyl group is an effective way to increase iodine concentration. Nitration of **1** and **2** leads to the formation of the previously inaccessible 3, 4-dinitro-5-iodopyrazole (**4**) and 1-methyl-3, 4-dinitro-5-iodopyrazole (**5**), respectively, giving rise to more energetic iodopyrazoles.

Our continuing interest in ADWs, led us to seek alternative and more lucrative routes to the synthesis of polyiodopyrazoles. Thus a recent report where it was possible to synthesize various polyiodobenzenes by employing molecular iodine under electrophilic conditions, appeared to be useful,[7] although the analytical purity of the products was not established using elemental analysis. Potassium persulfate was used as an oxidant in the presence of trifluoroacetic and sulfuric acids to generate the electrophilic species, I^+. It is likely that only highly stable substrates could survive under these harsh conditions thus suggesting pyrazoles known for their stability as excellent candidates for electrophilic substitution reactions.

Three equivalents of pyrazole or 1-methylpyrazole were treated with two equivalents of iodine in the presence of equal amounts of potassium persulfate in dichloroethane to obtain 3, 4, 5-triiodopyrazole (**1**) or 1-methyl-3, 4, 5-triiodopyrazole (**2**) in 63% and 82% yields, respectively. Compounds **1** and **2** were characterized by NMR, and IR spectra, elemental analysis, and DSC measurements (Scheme 1). The carbon-bonded methylene group in acetic acid is considered to be an active group for electrophilic nitration; it can be converted into the trinitromethyl group under nitrating conditions.[7] The 1-acetic acid substituent in pyrazole has a similar active methylene group, and although it seemed likely that it should be possible to generate the triiodomethyl moiety using electrophilic iodination, only 1-diiodomethyl-3, 4, 5-triiodopyrazole (**3**) was obtained in 30% yield (Scheme 1). It was fully characterized by using NMR, and IR spectra, elemental analysis, and DSC measurement techniques. Similar reactions with other heterocycles which contained the methylene group of acetic acid failed to react. However, apparently the nitrogen-linked acetic acid group has a sufficiently active methylene group for successful electrophilic iodination reactions under present conditions.

Table 1. Physical properties of compounds **1− 5**

Comp	T_m[a] [°C]	T_d[b] [°C]	d[c] [gcm^{-3}]	$\Delta H_f°$ [d] [kJ mol^{-1}]	$\Delta H_f°$ [kJ g^{-1}]	D[e] [ms^{-1}]	P[f] [GPa]	IS[g] [J]	Iodine [%]
1	224	272	3.38	461.1	1.03	2859	5.32	>40	85.4
2	154	-	3.35	307.2	0.66	2919	5.42	>40	82.8
3	-	371	3.94	453.1	0.63	2605	4.59	>40	89.2
4	150	292	2.46	621.6	2.19	5922	20.63	>40	44.7
5	81	363	2.30	644.8	2.16	6443	24.02	>40	42.6

[a] melting point; [b] decomposition temperature; [c] density - gas pycnometer (25°C); heat of formation - Gaussian 03; [e] calculated detonation velocity - Cheetah 6.0; [f] calculated detonation pressure - Cheetah 6.0; [g] impact sensitivities - BAM drop hammer.
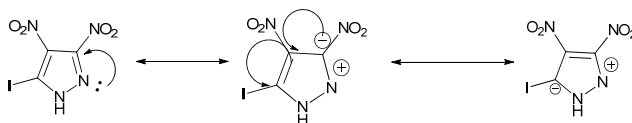
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After discovering a reliable synthetic route to 3, 4, 5-triiodopyrazole, attempts were made to introduce nitro groups onto the pyrazole ring.
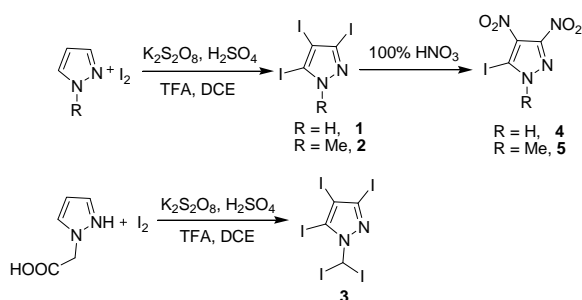
Scheme 1: Synthesis of **1-5**

Although a variety of nitrating conditions were tried, it was not possible to obtain the 3, 4, 5-substituted trinitropyrazole. However, nitration of 3, 4, 5-

triodopyrazole (**1**) or 1-methyl-3, 4, 5-triodopyrazole (**2**) with 100% nitric acid gave the new 3, 4-dinitro-5-iodopyrazole (**4**) or 1-methyl-3, 4-dinitro-5-iodopyrazole (**5**), respectively (Scheme 1), both of which previously had been inaccessible. Each was characterized by NMR, and IR spectra, elemental analysis and DSC measurement techniques. Single crystal structure analysis was carried out for **5**. Although **4** and **5** appeared to be susceptible to nucleophilic attack, e,g., to replace iodo at the 5-position, neither amination nor azidation of **4** and **5** under varying conditions was successful. This may arise from significant localization of a negative charge at position 5 in the ring thus enhancing the strength of the carbon-iodine bond and precluding substitution (Scheme 2).

Scheme 2: Delocalization of electrons in **4**

Heats of formation of all compounds were calculated with the Gaussian 03 program suite using isodesmic reactions [8] (Electronic Supporting Information Scheme S1). For these iodine-containing compounds, the (15s, 11p, 6d) basis of Strömberg et al. was augmented with other p shell and the five valence sp exponents optimized resulting in a [5211111111,411111111,3111] contraction scheme in conjunction with $6-31+G^{**}$ for first row and second row elements.[9] Single-point energy (SPE) refinement on the optimized geometries were performed with the use of $MP2/6-311++G^{**}$ level. Corresponding iodine sets were constructed in MP2 method by using all electron calculations and quasi relativistic energy-adjusted spin-orbit-averaged seven-valence-electron effective core potentials (ECPs). All compounds have positive heats of formation; as expected, **4** and **5** with nitro substituents have higher positive heats of formation. The calculated values for heats of formation and experimental densities were used to predict the detonation velocities (*D*) and detonation pressures (*P*) using the Cheetah 6.0 program. All the compounds have low detonation pressures which range from 4.59 to 24.02 GPa and the range of detonation velocities is 2605 to 6443 ms^{-1}.

The detonation products, I$_2$, and in some cases, HI, and I, which are strong biocides, were predicted using Cheetah 6.0 calculations. Compound **1** with one hydrogen atom was found to liberate HI while the other compounds do not liberate more than one percent HI or I. As shown in Figure 3, while compound **3** has the highest iodine concentration in its detonation products at ~89%, the detonation products of **1 - 3** each contains a high percentage of iodine that makes them good candidates as effective bio agent-defeat materials (Table 2).
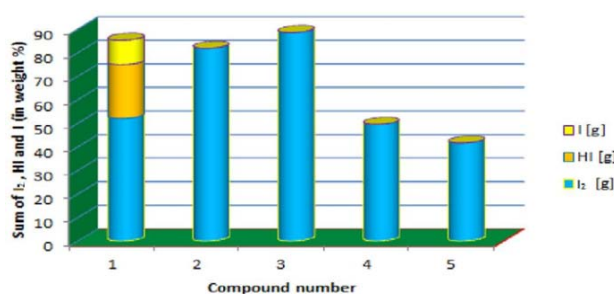
98

Figure 3: The sums of iodine-containing species in the detonation products of compounds 1, 2, 3, 4, and 5 (weight percent).

Table 1: Major detonation products shown by Cheetah 6.0 calculations [wt. % kg kg^{-1}]

Comp	N_2 [g]	I_2 [g]	HI [g]	I [g]	C [s]
1	6.22	52.1	22.87	10.34	8.00
2	6.09	81.9	-	-	8.51
3	3.93	88.6	-	-	6.34
4	22.2	49.6	-	-	8.36
5	18.8	41.7	-	-	5.07

The structure of **5** was obtained by X-ray single crystal crystallography. The crystallographic data are summarized in the Electronic Supporting Information. Suitable crystals were obtained by the slow evaporation of a solution of **5** in benzene and diethyl ether. The crystals are triclinic falling in the $P2_1$ space group with two molecules per crystal lattice (Figure 4). The bond length between N1 and N2 is 1.364(6) Å falling in the typical range of N–N single bonds (1.363(11)–1.366(12) Å).[10a] The distance between the C(4) ring carbon and nitrogen of the nitro group bonded to C(4) – N(8) is 1.419(8) Å. Similarly, the C(5) –N(11) bond length in 3, 4, 5-trinitropyrazole is 1.4538 (14) Å.[11] Thus the effect of iodine substituents is clearly seen in shortening of the C(4)-N(8) bond and lengthening of the C(5)-N(11) bond in comparison to similar bonds in 3, 4, 5-trinitropyrazole. The carbon-iodine bond length for C(3)-I(7) is 2.039(5) Å which is shorter than the normal carbon-iodine single bond length, 2.13 Å. [10]The shorter bond length may account for the failure of the amination or azidation reactions of **5.**
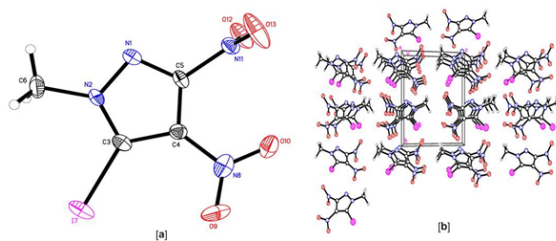

Figure 4: (a) Thermal ellipsoid plot (50%) of **5**. Hydrogen atoms are included but are unlabeled for clarity. (b) Ball and stack packing diagram of **5** viewed down the a-axis.

^{1}H and ^{13}C spectra were recorded on 300 MHz (Bruker Avance 300) nuclear magnetic resonance spectrometer operating at 300.13 and 75.48 MHz by using [D$_6$]DMSO as solvent and locking solvent unless otherwise stated. The chemical shifts in ^{1}H and ^{13}C spectra are reported relative to Me$_4$Si. The decomposition temperatures (onset) were obtained using a differential scanning calorimeter (TA Instruments Co., Model Q 10) at a scanning rate of 5 °C per minute in closed aluminum containers with a small hole in the lids. IR spectra were recorded using KBR pellets for solids on a BIORAD model 3000 FTS spectrometer. Densities were determined at room temperature employing a Micromeritics AccuPyic 1330 gas pycnometer. Elemental analyses were carried out using an Exeter CE-440 elemental analyzer

3, 4, 5-Triodopyrazole (**1**): A mixture of pyrazole (2 g, 29.3 mmol), iodine (12.4 g, 48.8 mmol) and potassium persulfate (13.1 g, 48.8 mmol) in dichloroethane (DCE, 50 mL) in a 500 mL round-bottomed flask was stirred in an ice bath for five minutes. Trifluoroacetic acid (39 mL) was added drop wise followed by concentrated sulfuric acid (1.75 mL). The reaction mixture was stirred for half an hour in an ice bath. After stirring at room temperature for fifteen minutes, the reaction mixture was heated for eight to twelve hours at 70-80 °C. The mixture was cooled to room temperature and the solvent was evaporated by blowing air on the solution The residue was washed with cold water and dissolved in ethanol with heating. The solution was filtered. Water (~ 15 mL) was added before evaporating the solution by blowing air to remove unreacted iodine. Finally the residue was again dissolved in ethanol and a little water was added. The solvent was removed using a rotary evaporator to give a white solid which was further washed with cold water to obtain a pure product (yield = 8.26g, 63.3%).

T_{melt} = 224.0 °C; T_{dec} (onset) = 272. 2 °C; IR (KBr) $\vee$ 3398, 3075, 2953, 2875, 2733, 1647, 1516, 1417, 1314, 1242, 1130,982, 961, 854, 449 cm^{-1} ; ^{1}H NMR δ 13.94 (broad, NH), 4.7 ; ^{13}C NMR δ 94.2, 85.1; elemental analysis: (%) calculated for C$_3$H I$_3$ N$_2$ (445.77): C, 8.08; H, 0.23; N, 6.28; found C, 8.27; H, 0.22; N, 6.20.

1-Diiodomethyl-3, 4, 5-triodopyrazole (**3**): Pyrazole-1-acetic acid was prepared according to the literature.[12] Pyrazole (12.5 g, 183.6 mmol) was added to sodium hydroxide (16.2 g, 405 mmol) dissolved in water (185 mL) in a one liter round-bottomed flask. Then bromoacetic acid (28.1 g, 202.2 mmol) was added in portions with stirring and the resulting mixture heated at reflux for 2 hours. After cooling, the mixture was carefully acidified (2 M HCl) to ~ pH 3 with vigorous stirring whereupon the product precipitated from the solution (Note: product does not precipitate if HCl is added too fast) (yield, 15.26 g, 67 %).

Pyrazole acetic acid (0.18 g, 1.5 mmol,), iodine (1.27 g, 5 mmol) was stirred for five minutes in a 100 mL round-bottomed flask and then trifluoroacetic acid (4 mL) was added drop wise followed by sulphuric acid (0.18 mL). The reaction mixture was stirred in an ice bath for ten minutes and at room temperature for half an hour. Then stirring continued at 70 °C to 80°C for forty-eight hours and allowed to cool to room temperature before pouring in ice-water. The residue was filtered and washed with cold water; dissolved in ethanol and ~ 5 mL water was added. Ethanol was removed by blowing air. The residue was filtered and washed with cold water (yield: 0.32 g, 30%).

T_{dec} (onset) = 371 °C; IR (KBr) v 3448, 2922, 1637, 1401, 1344, 1296, 1273, 1107,

983, 439 cm^{-1} ; ^{1}H NMR δ 13.61 (CHI$_2$) ; ^{13}C NMR δ 109.8, 107.4, 85.1, 83.9; elemental analysis: (%) calculated for C$_4$H I$_5$ N$_2$ (711.59): C, 6.75; H, 0.14; N, 3.94; found C, 6.94; H, 0.19; N, 4.89

3, 4-Dinitro-5-iodopyrazole (**4**): 3, 4, 5-Triiodopyrazole (5g. 11.2 mmol) was added portion wise to 100% nitric acid (50 mL) in 100 mL round-bottomed flask and the reaction mixture was stirred overnight at 100 °C. After cooling to room temperature the mixture was poured into crushed ice; the resulting solution was neutralized with solid sodium bicarbonate. The solution was acidified to pH 1 with concentrated hydrochloric acid and extracted with diethyl ether (3 x 20 mL). The combined extracts were washed with water and dried over anhydrous magnesium sulphate. A slightly yellow compound was obtained after evaporating the solvent using a rotary evaporator (yield, 2.3 g, 73.6%).

T_{melt} = 150.0 °C; T_{dec} (onset) = 291. 9 °C; IR (KBr) ν 3219, 1618, 1550, 1468, 1421, 1362, 1326, 1109, 790, 848, 814, 511 cm^{-1}; ^{13}C NMR δ 148.8, 129.6 91.7; elemental analysis: (%) calculated for C$_3$H I N$_4$ O$_4$ (283.97): C, 12.69; H, 0.35; N, 19.73; found C, 12.86; H, 0.37; N, 19.60.

3, 4-Dinitro-5-iodo-1-methylpyrazole (**5**): 1-Methyl-3, 4, 5-triodopyrazole (5 g, 10.8 mmol) was added portion wise to 100% nitric acid (50 mL) and the reaction mixture was stirred overnight at 100 °C. After cooling to room temperature, the mixture was poured into crushed ice to obtain a white precipitate. The mixture was filtered and the residue washed with cold water to leave a white solid   (yield, 2.3 g, 74%).

T_{melt} = 81.0 °C; T_{dec} (onset) = 363.0 °C; IR (KBr) ν 2924, 1554, 1531, 1491, 1454, 1413, 1355, 1325, 1229, 1124, 1080, 1020, 879, 808, 760, 732, 623 cm^{-1} ; ^{1}H NMR δ 4.0 (CH$_3$) ; ^{13}C NMR δ 147.9, 130.5, 96.7; elemental analysis: (%) calculated for C$_4$H$_3$ I N$_4$O$_4$ (298.00): C, 16.12; H, 1.01; N, 18.80; found C, 16.15; H, 0.91; N, 18.54.

Conclusions

Polyiodopyrazoles, 3, 4, 5-triiodopyrazole (**1**), 1-methyl-3, 4, 5-triiodopyrazole (**2**) and N-diiodomethyl-3, 4, 5-triiodopyrazole (**3**), were synthesized in efficient electrophilic reactions using molecular iodine in the presence of trifluoroacetic and sulphuric acid; the calculated detonation properties and products suggest that the compounds may be effective bio agent defeat agents. A synthetic method was developed as an effective strategy for introducing an N-diiodomethyl group into pyrazole. Nitration of **1** and **2** with 100% HNO$_3$ resulted in the formation of the heretofore inaccessible iodo dinitropyrazoles, **4** and **5**. These polyiodopyrazoles may have application not only as ADWs but also in other areas such as medicinal chemistry, materials science, and synthetic organic chemistry.

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